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(54) Title: PACKAGING THERMOPLASTICS FROM LACTIC ACID

(57) Abstract

A first general embodiment includes environmentally biodegradable compositions of poly(lactic acid) intimately plasticized with derivatives of oligomers of lactic acid, and mixtures such as lactic acid. A second general embodiment includes biodegradable polymer comprising polymerized lactic acid where the number of repeating lactic acid units n is an integer between 450 and 10,000 and the alpha carbon is a mixture of L- and D-configurations with a preponderance of either D- or L-units. A third general embodiment includes an environmentally degradable composition of blends of a physical mixture of poly(lactic acid), and a polymer selected from the group consisting of poly(ethylene terephthalate), a polymer or copolymer of styrene, ethylene, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof. A fourth general embodiment includes an environmentally degradable composition that comprises blends of a physical mixture of a poly(lactic acid), comprising about 1 to 99 weight percent of the composition, and an elastomeric blend compatible polymer.

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PACKAGING THERMOPLASTICS FROM LACTIC ACID

The present application is derived from and claims priority of the following four U.S. applications: the application entitled BIODEGRADABLE PACKAGING THERMOPLASTICS FROM POLYLACTIC ACID having Serial No. 07/579,005, filed September 6, 1990; the application entitled BIODEGRADABLE REPLACEMENT OF CRYSTAL POLYSTYRENE having Serial No. 07/579,465, filed September 6, 1990; the application entitled BLENDS OF POLYLACTIC ACID having Serial No. 07/579,000, filed September 6, 1990; and the application entitled DEGRADABLE IMPACT MODIFIED POLYLACTIC ACID having Serial No. 07/579,460, filed September 6, 1990; all of the above applications having Battelle Memorial Institute as assignee.

FIELD OF THE INVENTION

A first major embodiment of the present invention relates to plasticized biodegradable polymers of L-lactide, D-lactide, D,L-lactide and mixtures thereof suitable for packaging applications conventionally served by nondegradable plastics (e.g. polyethylene). This embodiment further relates to a method for producing pliable films and other packaging items from such polymers and to the unique product thereof. The invention has utility in producing a product that has the physical characteristics of the usual film forming plastics, yet is biodegradable.

The second major embodiment of this invention discloses a material and process of preparing it which is an offset, that is a replacement for crystal polystyrene, sometimes known as orientable polystyrene or OPS. The material is an offset for crystal polystyrene but is composed of a polyester capable of degrading in the environment over approximately one years time. The material is a polyester, comprised of polymerized lactic acid, prepared from either D-lactic acid or L-lactic acid,

and D,L-lactic acid. The ratio of the two polymerized monomer units, the process treatment and in some cases certain adjuvants, determine the precise physical properties required for the exacting requirements of a crystal polystyrene offset. Thus, at approximately a ratio of 90/10, L-lactic/D,L-lactic acid, the polymerized lactic acid (PLA) is a well behaved thermoplastic that is clear, colorless, and very stiff. As such it is very suitable for preparing films, foams, and other thermoformed items of disposable or one-way plastic. Having served its purpose as a packaging plastic, the poly(lactic acid) slowly environmentally biodegrades to innocuous products when left in the environment. This harmless disappearance can help alleviate the mounting problems of plastic pollution in the environment.

A third major embodiment of the invention relates to the blending of conventional thermoplastics with poly(lactic acid). This provides novel, environmentally degradable thermoplastics. The environmentally degradable thermoplastics are useful in a wide variety of applications.

A fourth major embodiment of the invention relates to the blending of compatible elastomers with polylactides. This provides impact-resistant modified poly(lactic acids) that are useful in a wide variety of applications including those where impact-modified polystyrene would be used.

BACKGROUND OF THE INVENTION

There is a need for an environmentally biodegradable packaging thermoplastic as an answer to the tremendous amounts of discarded plastic packaging materials. U.S. plastic sales in 1987 were 53.7 billion pounds of which 12.7 billion pounds were listed as plastics in packaging. A significant amount of this plastic is discarded and becomes a plastic pollutant that is a blot on the landscape and a threat to marine life.

Mortality estimates range as high as 1-2 million seabirds and 100,000 marine mammals per year.

A further problem with the disposal of plastic packaging is the concern for dwindling landfill space. It has been estimated that most major cities will have used up available landfills for solid waste disposal by the early 1990's. Plastics comprise approximately 3 percent by weight and 6 percent of the volume of solid waste.

One other disadvantage of conventional plastics is that they are ultimately derived from petroleum, which leaves plastics dependent on the uncertainties of foreign crude oil imports. A better feedstock would be one that derives from renewable, domestic resources.

However, there are good reasons for the use of packaging plastics. They provide appealing aesthetic qualities in the form of attractive packages which can be quickly fabricated and filled with specified units of products. The packages maintain cleanliness, storage stability, and desirable qualities such as transparency for inspection of contents. These packages are known for their low cost of production and chemical stability. This stability, however leads to very long life of plastic, so that when its one time use is completed, discarded packages remain on, and in, the environment for incalculably long times.

The polymers and copolymers of lactic acid have been known for some time as unique materials since they are biodegradable, biocompatible and thermoplastic. These polymers are well behaved thermoplastics, and are 100 percent biodegradable in an animal body via hydrolysis over a time period of several months to a year. In a wet environment they begin to show degradation after several weeks and disappear in about a year's time when left on or in the soil or seawater. The degradation products are lactic acid, carbon dioxide and water, all of which are harmless.

It will be appreciated by those skilled in the art that duplicating the properties of one thermoplastic with another is not predictable. Thus, with crystal polystyrene, there are exacting requirements for satisfactory performance of the polystyrene, which has been developed over many years to meet manufacturing and end-use specifications of crystal polystyrene grades.

In practice, lactic acid is converted to its cyclic dimer, lactide, which becomes the monomer for polymerization. Lactic acid is potentially available from inexpensive feedstocks such as cornstarch or corn syrup, by fermentation, or from petrochemical feedstocks such as ethylene. Lactide monomer is conveniently converted to resin by a catalyzed, melt polymerization, a general process well-known to plastics producers. By performing the polymerization from an intermediate monomer, versatility in the resin composition is permitted. Molecular weight can be easily controlled. Compositions can be varied to introduce specific properties.

Homopolymers and copolymers of various cyclic esters such as glycolide, lactide, and the lactones have been disclosed in numerous patents and scientific publications. Early patents disclosed processes for polymerizing lactic acid, lactide, or both, but did not achieve high molecular weight polymers with good physical properties, and the polymer products were frequently tacky, sticky materials. See, for example, U.S. Patents 1,995,970; 2,362,511; 2,683,136; and 3,565,869. The Lowe patent, U.S. Patent 2,668,162, teaches the use of pure glycolide and lactide to achieve high molecular weight polymers and copolymers of lactide. Copolymerization of lactide and glycolide imparted toughness and improved thermoplastic processability as compared to the homopolymers. Emphasis was placed on orientable, cold-drawable fibers. Films are described as self-supporting, or stiff, tough, and either clear or opaque. The polymers were high melting and stiff. U.S. patent 3,565,869 discloses the

typical attitude to the presence of monomer in polyglycolide—the removal of the monomer from the product. In U.S. 2,396,994, Filachione et al disclose a process for producing poly(lactic acids) of low molecular weights from lactic acid in the presence of a strong mineral acid catalyst. In U.S. 2,438,208, Filachione et al disclose a continuous process for preparing poly(lactic acid) with an acidic esterification catalyst. In U.S. 4,683,288, Tanaka et al disclose the polymerization or copolymerization of lactic and/or glycolic acid with a catalyst of acid clay, activated clay. The average molecular weight of the polymer is at least 5,000 and preferably 5,000-30,000. In U.S. 4,789,726, Hutchinson discloses a process for production of polylactides or poly (lactide-co-glycolide) of specified low-medium molecular weight, by controlled hydrolysis of a higher molecular weight polyester.

Similar disclosures in the patent and other literature developed the processes of polymerization and copolymerization of lactide to produce very strong, crystalline, orientable, stiff polymers which were fabricated into fibers and prosthetic devices that were biodegradable and biocompatible, sometimes called absorbable. The polymers slowly disappeared by hydrolysis. See, for example, U.S. Patents 2,703,316; 2,758,987; 3,297,033; 3,463,158; 3,498,957; 3,531,561; 3,620,218; 3,636,956; 3,736,646; 3,797,499; 3,839,297; 3,982,543; 4,243,775; 4,438,253; 4,496,446; 4,621,638; European Patent Application EP 0146398, International Application WO 86/00533, and West German Offenlegungsschrift DE 2118127 (1971). U.S. patents 4,539,981 and 4,550,449 to Tunc teaches high molecular weight materials suitable for prosthetic devices, while in EP 321,176 (1989) Tunc discloses a process for orienting resorbable thermoplastic members made from polylactides disclosed in the U.S. patents. U.S. patent 4,603,695 discloses sheet surgical adhesion preventatives. U.S. patent 4,534,349 discloses molded medical devices for

nerve repair. R.G. Sinclair et al in, Preparation and Evaluation of Glycolic and Lactic Acid-Based for Implant Devices Used in Management of Maxillofacial Trauma, I; AD748410, National Technical Information Service, prepares and evaluate polymers and copolymers of L-lactide and glycolide, the polymers were light brown in the case of the polyglycolide with increasing color in the case of the polymers incorporating more lactide, in a second series of polymers the homopolymer of lactide was a snow white crystalline solid.

Other patents teach the use of these polymers as stiff surgical elements for biomedical fasteners, screws, nails, pins, and bone plates. See, for example, U.S. Patents 3,739,773; 4,060,089; and 4,279,249.

Controlled release devices, using mixtures of bioactive substances with the polymers and copolymers of lactide and/or glycolide, have been disclosed. See, for example, U.S. Patents 3,773,919; 3,887,699; 4,273,920; 4,419,340; 4,471,077; 4,578,384; in 4,728,721, Yamamoto et al disclose the treatment of biodegradable high molecular weight polymers with water or a mixture of water and water soluble organic solvents so as to remove unreacted monomer or monomers and polymers of low polymerization degree. Poly(lactic acid) and copolymers of lactic and glycolic acid of 2,000 to 50,000 molecular weight are prepared by direct condensation for use as an excipient for microcapsules; R.G. Sinclair, in Environmental Science & Technology, 7 (10), 955 (1973). R.G. Sinclair, Proceedings, 5th International Symposium on Controlled Release of Bioactive Materials, 5.12 and 8.2, University of Akron Press, 1978. These applications of lactide polymers and copolymers required tough, or glassy materials, that were grindable and did not disclose physical properties for obvious use in thermoplastic packaging materials. R.G. Sinclair in, Lactic Acid Polymers--Controlled Release Applications for Biomedical Use and Pesticide Delivery; Proc. of the First Annual Corn

Util. Conf., p. 211, June 11-12, 1987, discusses some of the advantages of lactides as homopolymers and as copolymers with glycolide and caprolactones.

Some mention has been disclosed in the prior art for use of lactide copolymers for packaging applications. Thus, in the aforementioned patent to Lowe, clear, self-supporting films are noted of a copolymer of lactide and glycolide. In U.S. Patent 2,703,316 lactide polymers are described as film formers, which are tough and orientable. "Wrapping tissue" was disclosed that was tough, flexible, and strong, or pliable. However, to obtain pliability the polylactide must be wet with volatile solvent, otherwise, stiff and brittle polymers were obtained. This is an example of the prior art which teaches special modifications of lactide polymers to obtain pliability. U.S. Patent 2,758,987 discloses homopolymers of either L- or D,L-lactide which are described as melt-pressable into clear, strong, orientable films. The properties of the poly(L-lactide) are given as: tensile strength, 29,000 psi; percent elongation, 23 percent; and tensile modulus, 710,000 psi. The poly(D,L-lactide) properties were: 26,000 psi tensile strength; 48 percent elongation; and a tensile modulus of 260,000 psi. Copolymers of L- and D,L-lactide, that is copolymers of L- and D,L-lactic acid, are disclosed only for a 50/50 by weight mixture. Only tack point properties are given (Example 3). It was claimed that one antipodal (optically active, e.g., L-lactide) monomer species is preferred for the development of high strength. Thus, in U.S. Patent 3,021,309, lactides are copolymerized with delta valerolactone and caprolactone to modify lactide polymers and obtain tough, white, crystalline solids. Soft, solid copolymer compositions are mentioned only with the copolymer of caprolactone and 2,4-dimethyl-4-methoxymethyl-5-hydroxypentanoic acid lactone, not with lactide compositions. U.S. Patent 3,284,417 relates to the production of polyesters which are useful as plasticizers and intermediates for the

preparation of elastomers and foams. This patent excludes lactides and uses compositions based on 7- to 9-membered ring lactones, such as epsilon caprolactone, to obtain the desired intermediates. No tensile strength, modulus, or percent elongation data are given. U.S. Patent 3,297,033 teaches the use of glycolide and glycolide-lactide copolymers to prepare opaque materials, orientable into fibers suitable for sutures. It is stated that "plasticizers interfere with crystallinity, but are useful for sponge and films". Obvious in these disclosures is that the lactide polymers and copolymers are stiff unless plasticized. This is true also of U.S. Patent 3,736,646, where lactide-glycolide copolymers are softened by the use of solvents such as methylene chloride, xylene, or toluene. In U.S. Patent 3,797,499 copolymers of L-lactide and D,L-lactide are cited as possessing greater flexibility in drawn fibers for absorbable sutures. These fibers have strengths greater than 50,000 psi with elongation percentages of approximately 20 percent. In column 5, line 1, Schneider teaches against enhanced properties in the range provided in the present invention. Plasticizers such as glyceryl triacetate, ethyl benzoate and diethyl phthalate are used. Moduli are about one million psi. These are still quite stiff compositions compared to most flexible packaging compositions, reflecting their use for sutures. U.S. Patent 3,844,987 discloses the use of graft and blends of biodegradable polymers with naturally occurring biodegradable products, such as cellulosic materials, soya bean powder, rice hulls, and brewer's yeast, for articles of manufacture such as a container to hold a medium to germinate and grow seeds or seedlings. These articles of manufacture are not suitable for packaging applications.

U.S. Patents 3,297,033; 3,463,158; 3,531,561; 3,636,956; 3,736,646; 3,739,773; and 3,797,499 all disclose lactide polymers and copolymers that are strong crystalline, orientable polymers suitable for fibers and

suture materials. These disclosures teach the use of highly crystalline materials, which are oriented by drawing and annealing to obtain tensile strengths and moduli, typically, greater than 50,000 psi and 1,000,000 psi, respectively. Although formability is mentioned into a variety of shaped articles, physical properties of unoriented extrudates and moldings are not mentioned. For example, U.S. Patent 3,636,956 teaches the preparation of a copolymer having 85/15, 90/10, 92.5/7.5, or a 95/5 weight ratio of L-lactide/D,L-lactide; drawn, oriented fibers are cited; other plasticizers such as glyceryl triacetate, and dibutyl pthalate are taught; however, it is preferred in this disclosure to use pure L-lactide monomer for greater crystallinity and drawn fiber strength; and finally, the advantages of the present invention (e.g., an intimate dispersion of lactic acid-based plasticizers that provides unique physical properties) are not obtained.

U.S. Patent 4,620,999 discloses a biodegradable, disposable bag composition comprised of polymers of 3-hydroxybutyrate and 3-hydroxybutyrate/3-hydroxyvalerate copolymer. Lactic acid, by comparison, is 2-hydroxy propionic acid. U.S. Patent 3,982,543 teaches the use of volatile solvents as plasticizers with lactide copolymers to obtain pliability. U.S. Patents 4,045,418 and 4,057,537 rely on copolymerization of caprolactone with lactides, either L-lactide, or D,L-lactide, to obtain pliability. U.S. Patent 4,052,988 teaches the use of poly (p-dioxanone) to obtain improved knot tying and knot security for absorbable sutures. U.S. Patents 4,387,769 and 4,526,695 disclose the use of lactide and glycolide polymers and copolymers that are deformable, but only at elevated temperatures. European Patent Application 0108933 using a modification of glycolide copolymers with polyethylene glycol to obtain triblock copolymers which are taught as suture materials. As mentioned previously, there is a strong consensus that pliability is obtained in

lactide polymers only by plasticizers which are fugitive, volatile solvents, or other comonomer materials.

Copolymers of L-lactide and D,L-lactide are known from the prior art, but citations note that pliability is not an intrinsic physical property. The homopolymers of L-lactide and D,L-lactide, as well as the 75/25, 50/50, and 25/75, weight ratio, of L-/D,L-lactide copolymers are exampled in U.S. Patent 2,951,828. The copolymers have softening points of 110-135 C. No other physical property data are given relating to stiffness and flexibility. The 95/5, 92.5/7.5, 90/10, and 85/15, weight ratio, of L-lactide/D,L-lactide copolymers are cited in U.S. Patents 3,636,956 and 3,797,499. They are evaluated as filaments from drawn fibers and have tensile strengths in excess of 50,000 psi, moduli of about one million, and percent elongations of approximately 20 percent. Plasticizers, the same as in U.S. Patent 3,636,956, above, were used to impart pliability. A snow-white, obviously crystalline polymer, is cited in Offenlegungsschrift 2118127 for a 90/10, L-lactide/D,L-lactide copolymer. No physical properties were given for this copolymer. The patent teaches the use of surgical elements.

Canadian Patent 808,731 cites the copolymers of L- and D,L-lactide where a divalent metal of Group II is part of the structure. The 90/10, L-/D,L-lactide copolymer (Example 2) and the L-lactide homopolymer were described as "suitable for films and fibers". The 90/10 copolymer is described as a snow-white copolymer and the homopolymer of L-lactide can be molded to transparent films. (The more crystalline polymer should be the opaque, or snow-white material, which is the homopolymer.) The patent discloses "the fact that the novel polylactides of the present invention contain the metallic component of the catalyst in the form of a lactate is believed to be of significance". Furthermore, "the polylactides find utility in the manufacture of films and fibers which are prepared by conventional thermoplastic resin manufacturing

methods". No physical property data are given on the strength and flexibility of the films.

Canadian Patent 863,673 discloses compositions of L-lactide and D,L-lactide copolymers in the ratios of 97/3, 95/5, 92.5/7.5, 90/10, and 85/15 ratios of L-/D,L-lactide, respectively. These were all characterized as drawn filaments for surgical applications. Tensile strength, approximately 100,000 psi, was high, elongation was approximately 20 percent and plasticizers were mentioned to achieve pliability. D,L-lactide compositions of less than 15 weight percent are claimed.

Canadian Patent 923,245 discloses the copolymers of L- and D,L-lactide (Example 15). The 90/10 copolymer is described as a snow white polylactide. The polylactides prepared by the methods of the patent are stated to have utility in the manufacture of films or fibers prepared by conventional thermoplastic resin fabricating methods.

U.S. Patent 4,719,246 teaches the use of simple blending of poly L-and poly (D-lactide), referred to as poly (S-lactide) and poly (R-lactide). The examples are all physical mixtures. The special properties of the "interlocking" stem from racemic compound formation (cf. "Stereochemistry of Carbon Compounds", E. L. Eliel, McGraw-Hill, 1962, p. 45). Racemic compounds consist of interlocked enantiomers, that is, the D and L forms (or R and S) are bonded to each other by polar forces. This can cause a lowering, or raising, of the crystalline melting points, depending on whether the D to D (or L to L) forces are less, or greater, than the D to L forces. Required of polymer racemic compounds to enhance the effect (and stated in U.S. Patent 4,719,246, Column 4, line 48) are homopolymers, or long chain lengths, of both D and L. The great symmetry or regularity of these structures permit them to fit together, or interlock, by very regular polar forces, either because they are the same, or mirror images. This leads to considerable crystallinity. The

art of racemic compounds has a long history that goes back to classical chemistry.

Okuzumi et al, U.S. 4,137,921, in Example 4, teaches a 90/10 random copolymer of L-lactide and D,L-lactide, however, the advantages of the present invention are not obtained. Hutchinson, U.S. 4,789,726, teaches a process for the manufacture of polyesters, particularly polylactides of low molecular weight, by forming high molecular weight material and then degrading it to lower weight products of controlled polydispersity, however, monomers are removed in the process.

U.S. Patents 3,736,646; 3,773,919; 3,887,699; 4,273,920; 4,471,077; and 4,578,384 teach the use of lactide polymers and copolymers as sustained-drug release matrices that are biodegradable and biocompatible. Again, physical properties of the polymers from ordinary thermoforming methods such as film extrusion or molding are not mentioned.

Additional related art includes: Low molecular weight poly D,L-lactide has been recently added to high molecular weight D,L-lactide along with a drug such as caffeine, salicylic acid, or quinidine, see R. Bodmeier et al, International J. of Pharm. 51, pp. 1-8, (1989). Chabot et al in polymerizing L-lactide and racemic D,L-lactide for medical applications removed residual monomer and lower oligomers, see Polymer, Vol. 24, pp. 53-59, (1983). A.S. Chawla and Chang produced four different molecular weight D,L-lactide polymers but removed monomer for in vivo degradation studies, see Biomat., Med. Dev. Art. Org., 13(3&4), pp. 153-162, (1985-86). Kleine and Kleine produce several low residual monomer, poly(lactic acids) from D,L-lactide while determining lactide levels during the polymerization, see Macromolekulare Chemie, Vol. 30, pp. 23-38, (1959); Kohn et al also makes a low residual monomer product while monitoring the monomer content over time, see Journ. Appl. Polymer Science, Vol. 29, pp. 4265-4277, (1984). M. Vert et al teaches high

molecular weight polylactides with elimination of residual monomer, see Makromol. Chem., Suppl. 5, pp. 30-41, (1981). M. Vert, in Macromol. Chem.,Macromol. Symp. 6, pp.109-122, (1986), discloses similar poly(L-/D,L-lactide) polylactides, see Table 6, p. 118. In EP 311,065 (1989) poly D,L-lactide is prepared as an implant material for drug delivery as the material degrades, the material contains drugs, low molecular weight polylactide, and other additives; EP 314,245 (1989) teaches a polylactide having a low amount of residual monomer, the polymer is prepared by polymerization of meso D,L-lactide or other monomers; West German Offenlegungsschrift DE 3,820,299 (1988) teaches the polymerization of meso D,L-lactide with lactides, however, the advantages of the present invention are not obtained; and West German Offenlegungsschrift DE 3,820,299 (1988) teaches the polymerization of meso D,L-lactide with lactides; however, the advantages of the present invention are not obtained.

Of particular interest, U.S. patent 4,719,246 teaches the blending of homopolymers of L-lactide, D-lactide, polymers or mixtures thereof; and copolymers of L-lactide or D-lactide with at least one nonlactide comonomer. The blending is intended to produce compositions having interacting segments of poly(L-lactide) and poly(D-lactide).

U.S. 3,636,956 teaches an interweaving of fibers that is not blending or melt blending of a composition to make a physical mixture. U.S. patent 4,719,246 teaches the blending of homopolymers of L-lactide, D-lactide, polymers of mixtures thereof; and copolymers of L-lactide or D-lactide with at least one nonlactide comonomer. The blending is intended to produce compositions having interacting segments of poly(L-lactide) and poly(D-lactide). U.S. patent 4,661,530, discloses the mixtures of a poly (L-lactic acid) and/or poly (D,L-lactic acid) and segmented polyester urethanes or polyether urethanes. Biodegradable materials are formed that are useful in

synthetic replacements of biological tissues and organs in reconstructive surgery. PCT publication WO 87/00419 to Barrows reveals a bone spacer comprising a blend or mixture of a nonabsorbable polymer and a bioabsorbable polymer, polylactic acid is one of the preferred biodegradable polymers but plasticizers are not revealed therein. PCT publication WO 84/00303 to Gogolewski et al suggests blends of polyesters and polyurethanes for preparing surgical filaments. Cohn et al, in Biodegradable PEO/PLA Block Copolymers, Journal of Biomed. Mater. Res., Vol. 22, p. 993, 1988, reveals a physical mixture of poly(ethylene oxide) and poly(lactic acid).

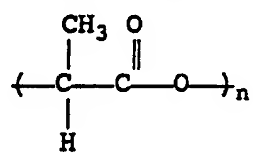
Nowhere in the prior art is it disclosed that lactic acid or lactide polymers can be the source of pliable, highly extensible compositions by the use of lactide monomers, or lactic acid, or oligomers of lactic acid, or derivatives of oligomers of lactic acid, or oligomers of lactide as the plasticizer. None of the prior compositions are suitable for well-defined packaging needs.

BRIEF DESCRIPTION OF THE INVENTION

A. The general teaching of the portion of the invention providing for flexible materials is that poly(lactic acids) derived from lactic acid (homopolymers or copolymers of L-lactic acid or D-lactic acid) or lactides (homopolymers or copolymers of L-lactide, D-lactide, meso D,L-lactide, and racemic D,L-lactide) that have been intimately plasticized with a plasticizer such as lactic acid, lactide, oligomers of lactic acid, oligomers of lactide, derivatives of oligomeric lactic acid, and various mixtures thereof, have utility as well behaved thermoplastics which can mimic properties of the usual environmentally very slowly degradable plastics, (e.g., the properties of polyethylene and the like). The term, intimately dispersed, as used herein means the material is homogeneously and intimately mixed with the

polymer. Since both lactic acid and lactide can achieve the same repeating unit, the general term poly(lactic acid) as used herein refers to polymers having the repeating unit of formula I without any limitation as to how the polymer was made (e.g. from lactides, lactic acid, or oligomers), and without reference to the degree of polymerization or level of plasticization.

In general, a first embodiment of the invention for flexible materials provides for an environmentally biodegradable composition useful as a replacement for thermoplastic polymer compositions comprising a poly(lactic acid) and a plasticizer selected from the groups below, wherein the plasticizer is intimately dispersed within the polymer. The poly(lactic acid) polymer has the repeating units of the formula,



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wherein n is the number of repeating units and n is an integer equal to at least about 150. Preferably the unoriented composition has the physical properties of: $150 \leq n \leq 20,000$, a tensile strength of about 300 to about 20,000 psi, an elongation to failure of about 50 to about 1,000 percent, and a tangent modulus of about 20,000 to about 250,000 psi. The intimate dispersion of the plasticizer can yield a substantially transparent composition, although transparency may not be obtained with certain processes, as when the composition is foamed.

In a further embodiment the composition can be a replacement for polyethylene when the unoriented composition has a tensile strength of about 1,200 to about 4,000 psi, an elongation to failure of about 100 to about 800 percent, and a tangent modulus of about 20,000 to about 75,000 psi. The composition can be a replacement for polypropylene when the unoriented composition has a tensile strength of about 4,500 to about 10,000 psi, an

elongation to failure of about 100 to about 600 percent, a tangent modulus of about 165,000 to about 225,000, and a melting point of about 150 to about 190 F.

A further embodiment of the invention provides a process for producing an environmentally biodegradable composition useful as a replacement for thermoplastic polymer compositions having the steps: (a) polymerizing a lactide monomer selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof, in the presence of a suitable catalyst; (b) controlling the polymerization to allow the reaction to be stopped prior to complete polymerization; (c) monitoring the level of remaining monomer; (d) stopping the polymerization prior to complete reaction so that unreacted monomer in a predetermined amount is trapped in association with the polymer; and (e) treating the polymer and unreacted monomer to obtain an intimately plasticized composition. The polymerization reaction is preferably stopped at a monomer level up to about 40 weight percent. If desired additional plasticizer may be incorporated into the composition prior to, during, or after the treating step, wherein the plasticizer is selected from the group of plasticizers discussed below. The sum of remaining monomer and additional plasticizer is preferably below about 40 weight percent and is most preferably between about 10 and about 40 weight percent for a pliable composition.

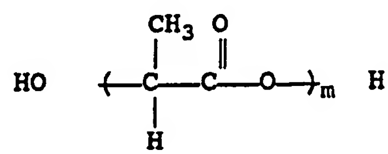
A yet further embodiment includes a process for producing a plasticized polymer of poly(lactic acid) that comprises mixing, heating, and melting one or more lactide monomers and a catalyst; polymerizing the monomers of the solution to form a polymer without stopping the reaction; and incorporating plasticizer as described below into the formed polymer.

A yet further embodiment includes a process for providing a poly(lactic acid) to which the above described

plasticizers may be added to obtain the desired properties.

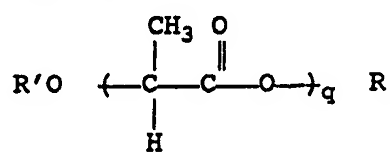
A yet further embodiment includes a process for the preparation of a biodegradable blown film through the inclusion of the below listed plasticizers in poly(lactic acid) to achieve desired properties followed by extrusion of the plasticized poly(lactic acid) as a blown film.

Plasticizers useful with the invention include lactic acid, lactide, oligomers of lactic acid, oligomers of lactide, and mixtures thereof. The preferred oligomers of lactic acid, and oligomers of lactide are defined by the formula:

 II

where m is an integer: $2 \leq m \leq 75$. Preferably m is an integer: $2 \leq m \leq 10$.

Further plasticizers useful in the invention include oligomeric derivatives of lactic acid, selected from the group defined by the formula:

 III

where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated,
where R′ = H, alkyl, aryl, alkylaryl or acetyl, and R′ is saturated,
where R and R′ cannot both be H, where q is an integer: $2 \leq q \leq 75$; and mixtures thereof. Preferably q is an integer: $2 \leq q \leq 10$.

For pliability, lactic acid or lactide monomer plasticizer is present in an amount of from about 10 to about 40 weight percent of the polymer, while plasticizers such as oligomers of lactide, or oligomers of lactic acid, and derivatives of oligomers of lactic acid may be present in an amount from about 10 to about 60 weight percent.

This composition allows many of the desirable characteristics of nondegradable polymers, e.g. polyethylene, such as pliability, transparency, and toughness. In addition, the presence of plasticizer facilitates melt processing, prevents discoloration, and enhances the degradation rate of the compositions in contact with the environment.

The intimately plasticized composition should be processed into a final product in a manner adapted to retain the plasticizer as an intimate dispersion in the polymer. The treatments to obtain an intimate dispersion include: (1) quenching the composition at a rate adapted to retain the plasticizer as an intimate dispersion; (2) melt processing and quenching the composition at a rate adapted to retain the plasticizer as an intimate dispersion; and (3) processing the composition into a final product in a manner adapted to maintain the plasticizer as an intimate dispersion.

The composition may comprise from about 2 to about 60 weight percent plasticizer. When a lactide is selected, the composition preferably comprises from about 10 to about 40 weight percent lactide plasticizer selected from the group consisting of lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof.

If desired, the plasticizer can be selected from the group of lactides consisting of D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide and mixtures thereof so that at least part of the lactide plasticizer is stereochemically different from the monomer used to prepare the polymer. Similarly the plasticizer may comprise oligomers of lactide, or oligomers of lactic acid, or mixtures thereof, having the formula II that are not produced during the production of the polymer.

Particularly advantageous is the sequential incorporation of plasticizer into poly(lactic acid) to obtain a blended composition by melt blending with the poly(lactic acid), a first plasticizer selected from the

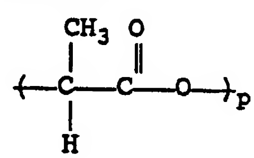
group consisting of oligomers of lactic acid, oligomers of lactide, and mixtures thereof; and melt blending with the blend a second plasticizer selected from the group consisting of lactic acid, L-lactide, D-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof. If desired, a first plasticizer defined by the formula III may be used alone or in admixture with an oligomer of formula II. This procedure allows the blending of the first plasticizer at a first temperature and the blending of the second plasticizer at a second temperature lower than the first temperature.

B. In general, a first embodiment of the invention for replacement of crystal polystyrene provides for an environmentally decomposable polymeric composition suitable for use as a substitute for crystal polystyrene. The composition comprises a poly(lactic acid), where the repeating unit is an L- or D-enantiomer and there is a preponderance of either enantiomer, having intimately dispersed therein a plasticizer, as described below, wherein the unoriented composition has the physical properties of a tensile strength of at least 5,000 psi, a tangent modulus of at least 200,000 psi, and is colorless. The composition can be adjusted to be form stable above about 70 C.

A further embodiment of the invention provides for a substitute for crystal polystyrene comprising a copolymer of the formula I: where n is an integer between about 450 and about 10,000; where the repeating unit is an L- or D-enantiomer and there is a preponderance of either enantiomer; and having intimately dispersed therein between about 0.1 and about 10 weight percent of a plasticizer, as described below, wherein the unoriented composition has the physical properties of a tensile strength of at least about 5,000 psi, a tangent modulus of at least about 200,000 psi, form stability above about 70 C, and is colorless. The ratio of L-enantiomer to D-enantiomer is preferably between about 99/1 and about 1/99

and most preferably between about 2.5/97.5 and 7.5/92.5, or between about 92.5/7.5 and 97.5/2.5.

A yet further embodiment of the invention provides a composition comprising a physical mixture of: (a) a first poly(lactic acid) having a preponderance of either D- or L- enantiomers; (b) a second poly(lactic acid) selected from the group consisting of poly(D-lactic acid) or a poly(L-lactic acid), wherein the weight percent ratio of the first poly(lactic acid) to the second poly(lactic acid) is between about 1/99 and 99/1; and (c) greater than about 0.1 weight perecent of plasticizer as described below, wherein the plasticizer is intimately dispersed within the poly(lactic acid); and the unoriented composition has a tensile strength of at least 5,000 psi and a tangent modulus of at least 200,000 psi, is form stable above 70 C, and is substantially colorless. Preferred ratios of the first and second polylactic acids are between about 98/2 to about 75/25, and most preferably between about 85/15 and about 95/5. The first poly(lactic acid) may be defined by formula I, where n is an integer between about 450 and about 10,000; and the second poly(lactic acid) by the formula:



IV

where p is an integer between about 450 and about 10,000; and the unoriented composition has the physical properties of a tensile strength of at least 5,000 psi, a tangent modulus of at least 200,000 psi, and is colorless. The composition of this embodiment may be oriented and annealed to provide a product having a plasticizer intimately dispersed within the poly(lactic acid), and the product has the physical properties of: a tensile strength in excess of 7,500 psi, a tangent modulus in excess of 350,000 psi, and dimensional heat stability at

temperatures above 70 C. The product can be biaxially oriented.

A yet further embodiment of the invention provides for an oriented and annealed environmentally decomposable film or sheet product suitable for use as a substitute for oriented crystal polystyrene film or sheet comprising: a film or sheet of a copolymer of the formula I: where n is between about 450 and about 10,000; where the repeating unit is an L- or D-enantiomer, and there is a preponderance of either enantiomer; the product having intimately dispersed therein the residue of a plasticizer, as described below; the oriented and annealed product having the physical properties of: a tensile strength in excess of 7,500, a tangent modulus in excess of 350,000, and dimensional heat stability at temperatures above about 70 C. The product may be biaxially oriented. Other embodiments of the product may contain the other plasticizers discussed below.

A further embodiment provides for an oriented and annealed environmentally decomposable film or sheet product suitable for use as a substitute for oriented crystal polystyrene film or sheet comprising: a physical mixture of between about 0.09 and about 99 weight percent of a poly(lactic acid) of the formula I: where n is an integer between about 450 and about 10,000 and having a preponderance of either the D- or the L-enantiomers; between about 99 and about 0.09 weight percent of a poly(lactic acid) of the formula IV: where p is an integer between about 450 and about 10,000, and the repeating unit is a D- or an L-enantiomer; below a plasticizer, as described below, intimately dispersed within the poly(lactic acid); and the product has the physical properties of: a tensile strength in excess of 7,500 psi, a tangent modulus in excess of 350,000 psi, and is dimensionally heat stable at temperatures above 70 C. The product may be biaxially oriented.

A further embodiment provides for an environmentally decomposable polymeric foam composition comprising a copolymer of the formula I: where n is an integer between about 450 and about 10,000, where the repeating unit is an L-or D-enantiomer and there is a preponderance of either enantiomer; having intimately dispersed therein a plasticizer discussed below and wherein the composition is form stable above 70 C.

A yet further embodiment of the invention provides for an environmentally decomposable polylactide product suitable as a substitute for crystal polystyrene comprising: a poly(lactic acid); and a plasticizer, as discussed below, intimately dispersed in the poly(lactic acid), wherein the poly(lactic acid) has a number average molecular weight, M_n, between about 50,000 and 400,000, a tensile strength of at least about 7500 psi and a tangent modulus of at least 350,000, form stability above 70 C, and is substantially clear and colorless after processing into a product.

Plasticizers contemplated for the compositions and processes in the present invention include: (a) lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, oligomers of lactic acid, oligomers of lactide, and mixtures thereof; where oligomers of lactic acid and oligomers of lactide defined by the formula II: where m is an integer: $2 \leq m \leq 75$; and (b) one or more derivatives of an oligomer of lactic acid defined by the formula III: where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated; where R′ = H, alkyl, aryl, alkylaryl or acetyl, and R′ is saturated; where R and R′ cannot both be H; and where q is an integer: $2 \leq q \leq 75$.

The plasticizers may be present as residual plasticizers from the polymerization reaction, or additional plasticizer that is added to the composition.

To obtain special compositions or processing characteristics the plasticizers may be present as: (a) a

first plasticizer selected from the group consisting of an oligomer of lactide, or an oligomer of lactic acid; and a second plasticizer selected from the group consisting of lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof; and (b) a first plasticizer selected from the group consisting of one or more derivatives of an oligomer of lactic acid defined by the formula III: where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated; where R' = H, alkyl, aryl, alkylaryl or acetyl, and R' is saturated; where R and R' cannot both be H; and where q is an integer: $2 \leq q \leq 75$; and a second plasticizer selected from the group consisting of lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof.

The amount of plasticizer present must be above about 0.1 weight percent. The upper limit is defined by the amount of plasticizer that will give the physical properties for crystal polystyrene as defined herein. A preferred amount of plasticizer is between about 0.1 weight percent and about 10 weight percent. The plasticizer may be added for example in an amount (1) effective to provide substantial transparency, (2) effective to prevent degradation during processing, and (3) effective to prevent discoloration during processing. The plasticizer may be added by methods known in the art for blending (e.g. mill blending) to obtain an intimate dispersion.

A yet further embodiment provides for a process for the manufacture of an environmentally decomposable film or sheet forming polymeric composition comprising: copolymerizing a molten blend of monomer selected from the group consisting of D-Lactide, L-lactide, D,L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof, wherein the monomers are selected to provide D- and L-enantiomers with a preponderance of either the D-, or L-enantiomer; terminating the polymerization reaction prior to completion to provide in the composition an

intimately dispersed plasticizer as discussed herein, the unoriented composition having a tensile strength of at least 5,000 psi and a tangent modulus of at least 200,000 psi; and treating the composition to maintain the plasticizer as an intimate dispersion within the polymer whereby a substantially colorless composition is obtained. If desired additional plasticizer may be added after the poymerization reaction is terminated. The composition may also be rendered transparent as described below.

The process preferably selects the type and amount of monomer to provide a ratio of L-enantiomer to D-enantiomer of between about 1/99 and 99/1. More preferably, the monomer is selected to obtain a ratio of L-enantiomer to D-enantiomer of between about 2.5/97.5 and 7.5/92.5 or between about 92.5/7.5 and 97.5/2.5. The process most preferably uses the selected monomers in the molten blend comprising between about 85 and 95 weight percent D-lactide or L-lactide, and between about 5 and 15 weight percent meso D,L-lactide or racemic D,L-lactide.

The polymeric composition may advantageously be extruded into a film or sheet and physically treated by orientation and/or annealing to provide a polymeric film or sheet having a tensile strength of at least 7,500 psi and a tangent modulus of at least 350,000 psi. An additional treatment comprises biaxially orienting and heat treating the polymeric composition.

The treatment may comprise adding nucleating agents, adding D-lactide or L-lactide homopolymer by blending, and orienting the polymer. Color bodies can be excluded by performing the polymerization in an inert atmosphere and at reaction temperatures below 140 C. If desired, the treatment step comprises annealing the composition above its glass transition temperature, whereby a higher heat deflection temperature is obtained.

C. A third general embodiment provides for an environmentally degradable composition comprising blends of a physical mixture of poly(lactic acid); one or more

polymers selected from the group consisting of a poly(ethylene terephthalate), a polymer or copolymer of styrene, ethylene, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof; and one or more plasticizers discussed below.

The poly(lactic acid) present in the blends may be represented by the formula I: where n is an integer between 75 and 10,000.

Plasticizers useful with the invention include D-lactic acid, L-lactic acid, racemic D,L-lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, oligomers of lactic acid, oligomers of lactide, and mixtures thereof. The oligomers of lactic acid and oligomers of lactide are defined by formula II: where m is an integer: $2 \leq m \leq 75$. Preferably m is an integer: $2 \leq m \leq 10$. These limits correspond to number average molecular weights below about 5,400 and below about 720, respectively.

Further plasticizers useful in the invention include oligomeric derivatives of lactic acid, selected from the group defined by formula III: where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated; where R′ = H, alkyl, aryl, alkylaryl or acetyl, and R′ is saturated; where R and R′ cannot both be H, where q is an integer: $2 \leq q \leq 75$; and mixtures thereof. Preferably q is an integer: $2 \leq q \leq 10$.

The plasticizers may be present in any amount that provides the desired characteristics. For example, the various types of plasticizers discussed herein and in the other general embodiments provide for: (a) more effective compatibilization of the melt blend components; (b) improved processing characteristics during the blending and processing steps; and (c) control and regulate the sensitivity and degradation of the polymer by moisture. For pliability, plasticizer is present in higher amounts while other characteristics are enhanced by

lower amounts. The compositions allow many of the desirable characteristics of pure nondegradable polymers. In addition, the presence of plasticizer facilitates melt processing, prevents discoloration, and enhances the degradation rate of the compositions in contact with the environment. The intimately plasticized composition should be processed into a final product in a manner adapted to retain the plasticizer as an intimate dispersion in the polymer for certain properties. These can include: (1) quenching the composition at a rate adapted to retain the plasticizer as an intimate dispersion; (2) melt processing and quenching the composition at a rate adapted to retain the plasticizer as an intimate dispersion; and (3) processing the composition into a final product in a manner adapted to maintain the plasticizer as an intimate dispersion. The plasticizers are preferably at least intimately dispersed within the polylactic acid if not in the coblended polymer.

Particularly advantageous is the sequential incorporation of plasticizer into poly(lactic acid) and the other polymer by melt blending with them a first plasticizer selected from the group consisting of oligomers of lactic acid, oligomers of lactide, and mixtures thereof; and melt blending with the blend a second plasticizer selected from the group consisting of lactic acid, L-lactide, D-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof. If desired, a first plasticizer defined by the formula III may be used alone or in admixture with an oligomer of formula II. This procedure allows the blending of the first plasticizer at a first temperature and the blending of the second plasticizer at a second temperature lower than the first temperature.

D. A fourth general embodiment provides for an environmentally degradable composition comprising blends of a physical mixture of poly(lactic acid) and blend-compatible elastomers that provide improved impact

resistance to the blended composition. Such an elastomer may be, for example, a Hytrel™: a segmented polyester which is a block copolymer of hard crystalline segments of poly(butylene terephthalate) and soft long chain segments of poly(ether glycol). One example is known by the trade name as Hytrel™ 4056 (DuPont) segmented polyester.

In addition to the above there are disclosed blends including one or more plasticizers. The blends are useful with the above materials, as well as with others as further discussed herein.

The poly(lactic acid) present in the blends may be represented by formula I: where n is an integer between 75 and 10,000.

Plasticizers useful with the invention include D-lactic acid, L-lactic acid, racemic D,L-lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, oligomers of lactic acid, oligomers of lactide, and mixtures thereof. The oligomers of lactic acid and oligomers of lactide are defined by formula II: where m is an integer: $2 \leq m \leq 75$. These limits correspond to number average molecular weights below about 5,400 and below about 720, respectively.

Further plasticizers useful in the invention include oligomeric derivatives of lactic acid, selected from the group defined by formula III: where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated; where R′ = H, alkyl, aryl, alkylaryl or acetyl, and R′ is saturated; where R and R′ cannot both be H; where q is an integer: $2 \leq q \leq 75$, and mixtures thereof.

The plasticizers may be present in any amount that provides the desired characteristics. For example, the various types of plasticizers discussed herein and in the other general embodiments provide for: (a) more effective compatibilization of the melt blend components; (b) improved processing characteristics during the blending and processing steps; and (c) control and regulate the sensitivity and degradation of the polymer by

moisture. For pliability, plasticizer is present in higher amounts while other characteristics are enhanced by lower amounts. The compositions allow many of the desirable characteristics of pure nondegradable polymers. In addition, the presence of plasticizer facilitates melt processing, prevents discoloration, and enhances the degradation rate of the compositions in contact with the environment. The intimately plasticized composition should be processed into a final product in a manner adapted to retain the plasticizer as an intimate dispersion in the polylactic acid and/or its coblended polymer for certain properties. These steps can include: (1) quenching the composition at a rate adapted to retain the plasticizer as an intimate dispersion; (2) melt processing and quenching the composition at a rate adapted to retain the plasticizer as an intimate dispersion; and (3) processing the composition into a final product in a manner adapted to maintain the plasticizer as an intimate dispersion.

Particularly advantageous is the sequential incorporation of plasticizer into poly(lactic acid) and the other polymer by melt blending with them, a first plasticizer selected from the group consisting of oligomers of lactic acid, oligomers of lactide, and .xtures thereof; and melt blending with the blend a second plasticizer selected from the group consisting of lactic acid, L-lactide, D-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof. If desired, a first plasticizer defined by the formula III may be used alone or in admixture with an oligomer of formula II. This procedure allows the blending of the first plasticizer at a first temperature and the blending of the second plasticizer at a second temperature lower than the first temperature.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a graph showing the relationship between percent lactide (abscissa X) in the composition as plasticizer and tensile strength measured in PSI (ordinate Y).

Figure 2 is a graph showing the relationship between weight percent lactide (abscissa X) in the composition as plasticizer and elastic modulus measured in 1000 PSI (ordinate Y).

Figure 3 is a graph showing the relationship between percent oligomer (abscissa X) in the composition as plasticizer and tensile strength measured in PSI (ordinate Y) where curve A is for a 90/10 copolymer and curve B is for a 92.5/7.5 copolymer.

Figure 4 is a graph showing the relationship between percent oligomer (abscissa X) in the composition as plasticizer and the elastic modulus measured in 1000 PSI (ordinate Y) where curve A is for a 90/10 copolymer and curve B is for a 92.5/7.5 copolymer.

Figure 5 is a graph showing a DSC plot of a control composition prepared by the teachings of the present invention. Temperature is measured in C (abscissa X); heat flow is measured in mW (ordinate Y). Curve A represents a first scan of the material and curve B the second scan.

Figure 6 is a graph showing a DSC plot of the composition of Example 80. Temperature is measured in C (abscissa X); heat flow is measured in mW (ordinate Y). Curve A represents a first scan and curve B the second scan.

Figure 7 is a graph showing a DSC plot of the composition of Example 81. Temperature is measured in C (abscissa X); heat flow is measured in mW (ordinate Y). Curve A represents a first scan of the material and curve B the second scan.

Figure 8 illustrates the differential scanning calorimetry (DSC) plot of unannealed 90/10, L-/D,L-lactide

copolymer of Example 5B. Temperature is measured in C (abscissa X); heat flow is measured in mW (ordinate Y). Curve A is unquenched copolymer; curve B is quenched copolymer.

Figure 9 illustrates the DSC plot of the material of Example 5B after remaining at 70 C for 100 minutes. Temperature is measured in C (abscissa X); heat flow is measured in mW (ordinate Y). Curve A is unquenched copolymer; curve B is quenched copolymer.

Figure 10 illustrates the DSC plot of the material of Example 5B after annealing in 185 F overnight. Temperature is measured in C (abscissa X); heat flow is measured in mW (ordinate Y). Curve A is unquenched copolymer.

Figure 11 illustrates the DSC plot of the material of Example 5B that has been blended with 5 percent calcium lactate. Temperature is measured in C (abscissa X); heat flow is measured in mW (ordinate Y). Curve A is unquenched copolymer; curve B is quenched copolymer.

Figure 12 compares the melt viscosity (poise) in thousands (ordinate Y) versus shear rate characteristics (1/sec) in thousands (abscissa X) of polystyrene (curve A) at C and the lactide polymer prepared as in Example 8B (curve B) at 160 C.

Figure 13 illustrates a DSC plot for the copolymer of Example 8B. Temperature is measured in C (abscissa X); heat flow is measured in mW (ordinate Y). Curve A is unquenched copolymer; curve B is quenched copolymer.

Figure 14 illustrates a DSC plot for the L-lactide homopolymer that is added to the copolymer of Example 8B. Temperature is measured in C (abscissa X); heat flow is measured in mW (ordinate Y). Curve A is unquenched homopolymer; curve B is quenched homopolymer.

Figure 15 illustrates a DSC plot for the blended composition of Example 23B of the copolymer of Example 8B

and a homopolymer of L-lactide. Temperature is measured in C (abscissa X); heat flow is measured in mW (ordinate Y). Curve A is the unquenched blend of copolymer and homopolymer; curve B is the quenched blend of copolymer and homopolymer.

Figure 16 illustrates a plot of the glass transition temperature of 90/10, L-/D,L-lactide copolymers versus residual lactide monomer. Abscissa X is lactide measured in wt.%; ordinate Y is T_g measured in C.

Figure 17 illustrates a DSC plot of 90/10, L-/D,L-lactide copolymer blended with 5 weight percent polystyrene. Temperature is measured in C (abscissa X); heat flow is measured in mW (ordinate Y). Curve A is the first heating; curve B is the second heating.

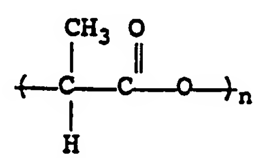
DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

A. First General Embodiment

The environmentally biodegradable compositions disclosed herein are completely degradable to environmentally acceptable and compatible materials. The intermediate products of the degradation: lactic acid and short chain oligomers of lactide or lactic acid are widely distributed naturally occurring substances that are easily metabolized by a wide variety of organisms. Their natural end degradation products are carbon dioxide and water. Contemplated equivalents of these compositions such as those that contain minor amounts of other materials, fillers, or extenders can also be completely environmentally degradable by proper choice of materials. The compositions herein provide environmentally acceptable materials because their physical deterioration and degradation is much more rapid and complete than the conventional nondegradable plastics that they replace. Further, since all or a major portion of the composition will be poly(lactic acid), and/or a lactic acid derived lactide or oligomer, no residue or only a small portion of

more slowly degrading residue will remain. This residue will have a higher surface area than the bulk product and an expected faster degradation rate.

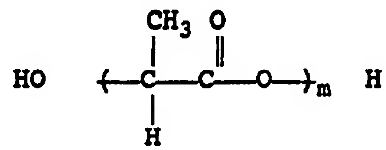
The general application of the invention results in the first and general embodiment of the invention. The homopolymers of D-lactide, L-lactide, D,L-lactide as well as copolymers of D-lactide, L-lactide; D-lactide, D,L-lactide; L-lactide, D,L-lactide; and D-lactide, L-lactide, and D,L-lactide all produce materials useful in the invention when plasticized by lactide monomers, lactic acid, oligomers of lactide, oligomers of lactic acid, derivatives of oligomeric lactide and mixtures thereof that are intimately dispersed in the polymer. A plasticizer may be produced by stopping the reaction before polymerization is completed. Optionally additional plasticizer consisting of lactide monomers (D-lactide, L-lactide, D,L-lactide, or mixtures thereof), lactic acid, oligomers lactide or oligomers of lactic acid or its derivatives including all L-, D-, and DL- configurations, and mixtures thereof can be added to the formed polymer. While aspects of the invention can be applied to various polylactides in general, one preferred polymer is defined by the formula:



I

where n is the degree of polymerization (number of repeating units), plasticized with a plasticizer derived from incomplete polymerization of the monomers used to produce the polymer. The more intimately the plasticizer is integrated within the polymer the better are its characteristics. In fact very intimate integration is needed to obtain the advantages of the invention further discussed below. If desired, additional monomer or oligomer plasticizer can be added to any residual monomer or oligomer remaining in the composition after

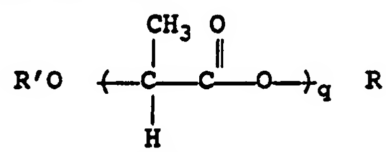
polymerization. The preferred oligomers of lactic acid, and oligomers of lactide including all L-, D-, DL- configurations and mixtures thereof, both random and block configurations, useful for a plasticizer are defined by the formula:



II

where m is an integer: $2 \leq m \leq 75$. Preferably m is an integer: $2 \leq m \leq 10$.

The oligomers of lactic acid and its derivatives including all L-, D-, DL- configurations and mixtures thereof, both random and block configurations, useful for a plasticizer are defined by the formula III:



III .

where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated,

and where R′ = H, alkyl, aryl, alkylaryl or acetyl, and R′ is saturated,

where R and R′ cannot both be H,

where q is an integer: $2 \leq q \leq 75$; and mixtures thereof. Preferably q is an integer: $2 \leq q \leq 10$.

The plasticizers added to the polymer compositions have the following functions:

(a) They act as plasticizers introducing pliability and flexibility into the polymer compositions not found in polymer-only composition.

(b) Addition of these plasticizers to the poly(lactic acid) reduces the melt viscosity of the polymers and lowers the temperature, pressure, and shear rate required to melt form the compositions.

(c) The plasticizers prevent heat build up and consequent discoloration and molecular weight decrease during extrusion forming of poly(lactic acid).

(d) The plasticizers add impact resistance to the compositions not found in the polymer alone.

In addition, the plasticizers may act as compatibilizers for melt-blends of polylactides and other degradable and nondegradable polymers. That is, molten mixtures of two different polymers can more intimately associate and mix into well-dispersed blends in the presence of the plasticizers. The plasticizers may also improve performance in solution blending.

The subscripts n, m, and q above refer to the average number of mers (the repeating unit) of the polymer or oligomer. Number average molecular weight M_n as used herein is related to the mers by multiplying n, m, or q by the molecular weight of the individual mer, for poly(lactic acid) this number is 72. The number of mers present in a polymer is also called the degree of polymerization. The reader is referred to the following texts where this subject is discussed further <u>Polymer Chemistry an Introduction</u>, 2nd Edition, R. Seymour et al, Marcel Dekker, Inc., 1988 and <u>Introduction to Polymer Chemistry</u>, R. Seymour, McGraw-Hill, New York, 1971.

The proportions of L-lactide, D-lactide, and D,L-lactide in the polymer are not critical to obtaining flexible thermoplastics; however, the proportions of D,L-lactide may vary certain properties as further discussed below. The parts of L-lactide, D-lactide, and D,L-lactide can vary over a wide, weight-ratio to form a homopolymer or copolymer. The lactide monomers employed in accordance with the invention are available commercially so that neither the monomeric reactant per se nor the method by which it is prepared constitute any portion of the invention.

D-lactide is a dilactone, or cyclic dimer, of D-lactic acid. Similarly, L-lactide is a cyclic dimer of L-lactic acid. Meso D,L-lactide is a cyclic dimer of D- and L-lactic acid. Racemic D,L-lactide comprises a mixture of D-lactide and L-lactide. When used alone herein, the term "D,L-lactide" is intended to include meso D,L-lactide or racemic D,L-lactide.

One of the methods reported in the literature for preparing a lactide is to dehydrate lactic acid under high vacuum. The product is distilled at a high temperature and low pressure. Lactides and their preparation are discussed by W. H. Carothers, G. L. Dorough and M. J. Johnson (J. Am. Chem. Soc. 54, 761-762 [1932]); J. Gay-Lussac and J. Pelouse (Ann. 7, 43 [1833]); C. A. Bischoff and P. Walden (Chem. Ber. 26, 263 [1903]; Ann. 279, 171 [1984]); and Heinrich Byk (Ger. Pat. 267,826 [1912]); through Chem. Abstr. 8, 554, 2034 [1914]).

The optically active acids can be prepared by direct fermentation of almost any nontoxic carbohydrate product, by-product or waste, utilizing numerous strains of the bacterial genus Lactobacillus, e.g. Lactobacillus delbrueckii, L. salivarius, L. casei, etc. The optically active acids can also be obtained by the resolution of the racemic mixture through the zinc ammonium salt, or the salt with alkaloids, such as morphine. L-lactide is a white powder having a molecular weight of 144. If an impure, commercially-available product is employed in accordance with the present invention, it is preferable to purify it by recrystallization from anhydrous methyl isobutyl ketone. The snow-white crystals of L-lactide melt at 96-98 C. As used herein the symbol C denotes degrees Centigrade and replaces the symbol °C, similarly the symbol F denotes degrees Fahrenheit and replaces the symbol °F.

D,L-lactic acid which is used in the preparation of D,L-lactide is available commercially. The D,L-lactic acid can be prepared synthetically by the hydrolysis of

lactonitrile (acetaldehyde cyanohydrin) or by direct fermentation of almost any nontoxic carbohydrate product, by-product or waste, utilizing numerous strains of the bacterial genus Lactobacillus. D,L-lactide is a white powder having a molecular weight of 144. If an impure, commercially-available product is employed in accordance with the present invention, I prefer to purify it by recrystallization from anhydrous methyl isobutyl ketone. One such commercially available product comprising a mushy semisolid melting at 90-130 C was recrystallized from methyl isobutyl ketone and decolorized using charcoal. After three such recrystallizations, the product was tumble-dried in vacuo under a nitrogen bleed for 8 to 24 hours at room temperature. The snow white crystals thus obtained comprise a D,L-lactide mixture melting from 115-128 C.

In preparing the compositions in accordance with the invention, it is preferred to carry out the reaction in the liquid phase in a closed, evacuated vessel in the presence of a tin ester of a carboxylic acid containing up to 18 carbon atoms. The compositions, however, can also be prepared at atmospheric pressure with the polymerization system blanketed by an inert gas such as, for example, nitrogen. If polymerization is conducted in the presence of oxygen or air, some discoloration occurs with a resulting decrease in molecular weight and tensile strength. The process can be carried out at temperatures where the polymerization is sluggish in its later stages so as to trap residual monomer in the viscous polymer melt. Preferred temperatures for this purpose are generally between the melting points of pure L-lactide and pure D,L-lactide, or between 95 to 127 C. While in no way wishing to limit the scope of the invention, it is presently believed that below about 129 C, the following occurs:

1. The reactant lactide monomer mixture of L- and D,L-lactide monomers melt to form a

eutectic mixture, which melts to a mobile fluid that is an intimate solution of one, two, or three monomers.

2. The fluid melt is polymerized by catalyst to form an increasingly viscous solution and eventually unreacted monomer is trapped in association with the polymer as a solution, rather than as a distinct heterogeneous phase. The monomer no longer can react since the reaction is extremely diffusion controlled and cannot efficiently contact the low concentration of active end-groups of the polymer.
3. The polymerization ceases or slows considerably so that at room temperature the blend of monomer and polymer are a solid solution that imparts plasticization, clarity, and flexibility to the composition.
4. The catalyst deactivates so that subsequent melt-fabrication does not reinitiate the polymerization.
5. The plasticized composition is quite stable since the residual monomer is very high boiling, e.g., lactide has a boiling point of 142 C at 8 torr, and is tightly associated with its open-chain tautomer, polylactide.

Alternatively, the process can be carried out at any temperature between the melting point of the L-lactide and 200 C and lactic acid or lactide is subsequently melt or solvent-blended into the polymer as a further processing step. Temperatures above 200 C are undesirable because of the tendency of the copolymer to be degraded. Increasing the temperature within the range of 95 to 200 C generally increases the speed of the polymerization. Good results

are obtained by heating a mixture of L-lactide and D,L-lactide at a temperature between about 110 C and 160 C.

The catalysts employed in accordance with the invention are tin salts and esters of carboxylic acids containing up to 18 carbon atoms. Examples of such acids are formic, acetic, propionic, butyric, valeric, caproic, caprylic, pelargonic, capric, lauric, myristic, palmitic, stearic and benzoic acids. Good results have been obtained with stannous acetate and stannous caprylate.

The catalyst is used in normal catalytic amounts. In general, a catalyst concentration in the range of about 0.001 to about 2 percent by weight, based on the total weight of the L-lactide and D,L-lactide is suitable. A catalyst concentration in the range of about 0.01 to about 1.0 percent by weight is preferred. Good results were obtained when the catalyst concentration is in the range of about 0.02 to about 0.5 percent by weight. The exact amount of catalyst in any particular case depends to a large extent upon the catalyst employed and the operating variables including time and temperature. The exact conditions can be easily determined by those skilled in the art.

The reaction time of the polymerization step, per se, is governed by the other reaction variables including the reaction temperature, the particular catalyst, the amount of catalyst and whether a liquid vehicle is employed. The reaction time can vary from a matter of minutes to a period of hours, or days, depending upon the particular set of conditions which are employed. Heating of the mixture of monomers is continued until the desired level of polymerization is detected. The level of polymerization can be determined by analysis for residual monomers. As discussed previously, the reaction temperature can be chosen to enhance the incorporation of monomer and provide plasticized compositions coming directly out of the polymerization reactor. The reaction can be halted at such time that the composition has

attained the conversion of monomer to polymer that is desired to achieve the desired plasticization. In the preferred embodiment of the invention, approximately 2 to 30 percent lactide is left unreacted, depending on the degree of plasticization to be achieved.

In general it is preferred to conduct the polymerization in the absence of impurities which contain active hydrogen since the presence of such impurities tends to deactivate the catalyst and/or increase the reaction time. It is also preferred to conduct the polymerization under substantially anhydrous conditions.

The copolymers of the invention can be prepared by bulk polymerization, suspension polymerization or solution polymerization. The polymerization can be carried out in the presence of an inert normally-liquid organic vehicle such as, for example, aromatic hydrocarbons, e.g., benzene, toluene, xylene, ethylbenzene and the like; oxygenated organic compounds such as anisole, the dimethyl and diethyl esters of ethylene glycol; normally-liquid saturated hydrocarbons including open chain, cyclic and alkyl-substituted cyclic saturated hydrocarbons such as hexane, heptane, cyclohexane, alkylcyclohexanes, decahydronaphthalene and the like.

The polymerization process can be conducted in a batch, semi-continuous, or continuous manner. In preparing the lactide monomeric reactants and catalyst for subsequent polymerization, they can be admixed in any order according to known polymerization techniques. Thus, the catalyst can be added to either of the monomeric reactants. Thereafter, the catalyst-containing monomer can be admixed with the other monomer. In the alternative, the monomeric reactants can be admixed with each other. The catalyst can then be added to the reactant mixture. If desired, the catalyst can be dissolved or suspended in an inert normally-liquid organic vehicle. If desired, the monomeric reactants either as a solution or a suspension in an inert organic vehicle can

be added to the catalyst, catalyst solution or catalyst suspension. Still further, the catalyst and the monomeric reactants can be added to a reaction vessel simultaneously. The reaction vessel can be equipped with a conventional heat exchanger and/or a mixing device. The reaction vessel can be any equipment normally employed in the art of making polymers. One suitable vessel, for example, is a stainless steel vessel.

The environmentally biodegradable compositions produced in accordance with the present invention depending upon the L-lactide, D-lactide, meso D,L-lactide ratios, find utility in articles of manufacture, such as films, fibers, moldings and laminates, which are prepared by conventional fabricating methods. These articles of manufacture are contemplated for nonmedical uses i.e. outside the body where they can substitute for the common environmentally nondegradable plastics.

Filaments, for example, are formed by melt-extruding the copolymer through a spinneret. Films are formed by casting solutions of the biodegradable compositions and then removing the solvent, by pressing solid biodegradable compositions in a hydraulic press having heated platens, or by extrusion through a die, including Blown Film techniques.

Various techniques including melt blending, slow cooling, and rapid cooling (quenching) can be employed in preparing products e.g. moldings from the polymers and copolymers of the invention.

Quenching as used herein indicates that the temperature is dropped rapidly to prevent extensive crystallization of the polymer. Crystallization of polymers is a slow process, requiring minutes to hours to fully accomplish. When this is desired, the temperature is held above the glass-transition temperature, Tg, for some time to allow the molecules to order themselves into extensive crystalline lattices. This is called annealing. When cooled rapidly from an amorphous melt, the polymer

does not have the time required and remains largely amorphous. The time required to quench depends on the thickness of the sample, its molecular weight, melt viscosity, composition, and its Tg, where it is frozen-in as a glassy state. Note that melt viscosity and Tg are lowered by plasticization and favor quenching. Thin films obviously cool very quickly because of their high surface-to-volume ratio while molded items cool more slowly with their greater thicknesses and time spent in a warm mold before removal. Regular structures such as poly (L-lactide) order more easily and crystallize more quickly than more random structures such as a copolymer.

With the polylactides the melting points are approximately 150-190 C depending on the L-lactide content and, therefore, the regularity of structure. The Tg of all the polylactides, including various L and D,L homopolymers and copolymers is 60 C. The Tg decreases when residual lactide is intimately dispersed with the polymer. Quenching to an amorphous state requires that the polymer or copolymer in an amorphous melt is rapidly cooled from its molten state to a temperature below its Tg. Failure to do so allows spherulitic crystallinity to develop, that is, crystalline domains of submicron to micron size. The latter scatters light and the polymer specimens become opaque. These crystalline forms have improved stability to heat distortion. This spherulitic crystallinity is often called short range order-long range disorder since the crystallites are separated by amorphous regions. However, the crystallites act as pseudo crosslinks to maintain dimensional stability above the Tg but below their melting points. Alternatively stability to heat distortion can be obtained by orienting an amorphous polymer above its Tg but below its melting point. Here, the polymer molecules are stretched to allow some long range ordering, then "heat set" to permit the ordering to complete, that is, given some time to anneal. The amorphous polymer is thereby crystallized into a

different order, called long-range order, short range disorder. Transparency and resistance to heat distortion are favored.

A detailed discussion can be found in textbooks, for example, "Structural Polymer Properties", by Robert J. Samuels, Wiley Publications, NY, NY 1974.

Contemplated equivalents of the compositions of the invention are those that contain minor amounts of other materials. The copolymers produced in accordance with the present invention can be modified, if desired, by the addition of a cross-linking agent, other plasticizers, a coloring agent, a filler and the like, or minor amounts of other lactone monomers such as glycolide or caprolactone.

Cross-linking can be effected by compounding the compositions with free-radical initiators such as cumene hydroperoxide and then molding at elevated temperatures. This can improve heat-and solvent-resistance. Curing can also be effected by compounding the copolymers with multifunctional compounds such as polyhydric alcohols and molding, or thermoforming under heat and vacuum. Graft-extruder reactions to effect curing of the polyesters is an obvious method of cross-linking and chain-extending the copolymers.

In preparing moldings, a filler can be incorporated in the compositions prior to curing. A filler has the function of modifying the properties of a molding, including hardness, strength, temperature resistance, etc. Known filler materials include aluminum powder, powdered calcium carbonate, silica, kaolinite (clay), magnesium silicate and the like. Of particular advantage is starch, which blends well with the compositions to obtain a blend which is totally environmentally biodegradable. Other property modifications can be effected by melt blending the compositions with other polymers and copolymers of the lactides, glycolides, and caprolactone.

The compositions prepared according to the present invention can be used in producing reinforced laminates according to known procedures. In general, laminates are made from a fibrous mat or by assembling a multiplicity of sheets of material to form a matrix which is consolidated into a unitary structure by flowing molten precursor or composition through the fibrous material and curing it while in a mold or hydraulic press to form the polymer. Fibers which are used in forming the matrix include natural and synthetic fibers such as cellulose derived from wood, cotton, linen, hemp, and the like, glass, nylon, cellulose acetate and the like.

The compositions of the first general embodiment and their preparation are further illustrated by the following specific examples.

Example 1

80/20, L-lactide/racemic D,L-lactide

160 grams of L-lactide and 40 grams of racemic D,L-lactide, both of high purity (Purac, Inc., triply recrystallized), were charged into a 500 ml, round-bottom flask and purged with dry nitrogen overnight. 10 ml of stannous octoate is dissolved in 60 ml of anhydrous toluene, and 10 ml of the solvent is distilled to a Dean-Stark trap to effect dryness of this catalyst solution by azeotropic distillation. From the 10 ml of stannous octoate in 50 ml of dry toluene a 0.20 ml portion is removed with a syringe and injected into the lactides in the reaction flask. The nitrogen purge is continuous via a syringe needle connection that enters the reaction flask through a rubber septum and vents via a piece of tubing that connects to a bubbler. The nitrogen flow is maintained at 1-3 bubbles per second. The flask was heated in an oil bath maintained at 123-127 C. During the first part of the heating the lactides melt and are mixed thoroughly by swirling. Thereafter, the products become quite viscous. After 20 hours of heating, the flask and

the colorless, transparent products are removed from the heating bath, cooled, the flask broken, and shocked with liquid nitrogen to remove glass from the product. The copolymer was molded in a heated hydraulic press. Compression molding to 5- to 10-mil thick films was possible at 20,000 lb pressure, at 170 C, in a time period of 2 minutes. The films were evaluated for their tensile properties on a Instron tester, and the results are listed in Table 1. Samples 1/8-inch thick were also molded for impact strength testing. A thermogravimetric analysis of the product was performed, noting the weight loss upon heating the sample to 150 C in 4 minutes and holding the temperature at 150 C for 60 minutes. The weight loss of the sample was 19.5 percent and nearly complete in 60 minutes. The weight loss is attributed to loss of lactide monomer. Results of differential scanning calorimetry reveal that the composition has an endotherm beginning about 110 C, becoming more pronounced as the temperature increases to 200 C. No melting point was observed. Specimens were annealed at 185 F overnight and reexamined. They remained transparent, colorless and pliable. Samples of the copolymer could be remolded 6 times without any discoloration or obvious loss of strength. Thin films were clear, transparent, colorless, and quite flexible, despite the repeated molding.

TABLE 1. PROPERTIES OF COPOLYMERS[a] OF L-LACTIDE AND D,L-LACTIDE WHEN PLASTICIZED BY LACTIDE

Example	1	2	3
Film thickness, mil	8	8	10
Tensile strength, 1000 psi, ASTM D638	3.9	1.7	7.9
Elongation, percent	280	806	3.5
100 percent modulus, 1000 psi	0.75	--	--
200 percent modulus, 1000 psi	1.20	--	--
Tangent modulus, 1000 psi	36.6	--	289
Izod impact strength, ft-lb/in.[b]	0.63	--	0.4
M_w, 1000's	540	281	341
M_n, 1000's	270	118	97.5
Residual lactide[c], percent	19.5	27.8	2.7

[a] 80/20, weight ratio, of L-/racemic D,L-lactide
[b] 1/8-inch, notched samples
[c] By isothermal thermogravimetric analysis weight loss at 150 C

Example 2

In a 3-liter, round-bottom flask was charged 1.84 Kg of L-lactide, 0.46 Kg of racemic D,L-lactide and 2.3 ml of the stannous octoate solution, similar to Example 1. The mixture was purged with argon for 3 hours, then heated isothermally in a 125 C oil bath. The mixture melts, was mixed thoroughly by swirling, and forms a homogeneous, transparent, colorless fluid whose viscosity increases substantially after several hours. After 64 hours the flask was removed from the heating bath, cooled, and the glass removed from the clear, transparent, solid product. The rubbery composition was guillotined into slices and ground to 1/8 inch, or smaller, size in a grinder with dry ice. The grind was dried in an air circulating oven at 100 F for several hours, then vacuum dried overnight at ambient temperature. Compression-molded films were

prepared as described in Example 1 and the films were examined for their tensile properties and weight loss by thermogravimetric analysis as shown in Table 1.

Example 3

In a 250-ml, round bottom flask was placed 79.98 g of L-lactide, 20.04 g of racemic D,L-lactide, and 0.20 ml of stannous octoate solution, similar to Example 1. The flask was swept by nitrogen through inlets and outlets and heated in a 125 C oil bath. The mixture melted to a colorless and fluid liquid that was thoroughly mixed by swirling the flask. After 2 hours, the oil bath temperature was increased to 147 C, and after 14 hours total heating time, the temperature was decreased to 131 C. Total heating time was 18 hours. The product is transparent, colorless, and glassy. It was evaluated, similar to the preceding examples and the results are recorded in Table 1.

Examples 1 to 3 reveal the effect of reaction temperature on the properties of the copolymers as occasioned by the resulting composition.

Example 4

Films of the copolymers of Examples 1 and 3 were immersed in water for several months. After 3 weeks, the copolymer of Example 1 became hazy while that of Example 3 remained clear for approximately 2 months; after 3 months the film of Example 3 became noticeably hazy and the film of Example 1 is white and opaque. The water that had been in contact with the film of Example 1 tastes acidic while that of Example 3 is tasteless.

Inspection of the data of Table 1 reveals that the copolymer of Example 1 is an environmentally biodegradable replacement for polyethylene. Those skilled in the art will recognize that the physical properties of the copolymer are an excellent combination useful for many packaging applications. Its tensile strength and initial

tangent modulus compare favorably with polyethylene compositions used, for example, in plastic trash bags, general film wrap, plastic shopping bags, sandwich wrap, six pack yokes and the like. The shape of the stress-strain curves are approximately the same for both the copolymer and that for a linear low density polyethylene composition commonly used in trash bag compositions. A comparison of properties are shown in Table 2.

TABLE 2. COMPARISON OF POLYETHYLENE TO POLYLACTIC ACID

Property	LDPE-[a] NA 272	LLDPE[b]	Lactide Copolymer[c]
Tensile strength, 1000 psi, ASTM Standard C	2.18	2.9	3.9
Elongation, %	261	500	280
Tangent modulus, 1000 psi	54.9	51.0	36.6
100% modulus, 1000 psi	1.77	--	0.74
200% modulus	1.82	--	1.20
HDT[d], 264 psi, F	95	99	122

[a] Linear low-density polyethylene, 5-10 mil, 2-in./min., our experiments.
[b] Linear low-density polyethylene, data from computer file.
[c] Copolymer of L-lactide/racemic D,L-lactide, Example 1.
[d] Heat deflection temperature.

The lactide polymerization can be stopped at incomplete monomer-to-polymer conversion in a controllable fashion. This is illustrated in Examples 1 and 2. The lactide monomer binds very intimately with polymers of lactides. Alternatively, the compositions can be derived by mixing of lactide with preformed polymer. In that case, the lactide added can be the same or different with respect to stereochemistry, i.e., L-, D-, or D,L-lactide to that used to make the polymer.

The compounding can be accomplished by blending the molten polymer with lactide monomer in conventional processing equipment such as a mill roll or a twin screw compounder. The normally stiff, glassy, lactide polymers are flexibilized by the lactide and remain transparent, colorless, and very nearly odorless. The lactide is not very fugitive, requiring heating, and a nitrogen sweep, typically, 170-200 C for 20-60 minutes to remove the lactide in a gravimetric analysis. Neither is the lactide visible in films under an optical microscope. The lactide domains are submicron in size. This flexibilizing of the poly(lactic acid) suggests its use as a environmentally biodegradable replacement for polyolefin, disposable, packaging films.

Examples 5-16

A series of experiments were performed in which copolymers of L- and racemic D,L-lactide were prepared, melt blended with variable amounts of lactide, and the physical properties of the blends evaluated as a function of the lactide composition. Monomer lactide content was assayed by a previously developed isothermal, thermogravimetric analysis. The lactide contents were measured before and after compounding and molding into films.

It was observed that open roll, 2 roll, milling tended to volatilize the lactide at temperatures required for the very high, molecular weight lactide copolymers. These losses could be minimized by masterbatching or by using lower molecular weight lactide copolymers (and their lower attendant mixing temperatures). A better mixing and blending method was a conventional, twin screw extruder, which minimized volatile losses. Some results are shown in Table 3.

Alternatively, a mixture of oligomeric lactic acid, or a derivative of an oligomer of lactic acid, oligomeric lactic acid and lactide can be used to prepare

a flexible film, whereby the oligomers or their derivatives are added first, allowing the lactide to be mixed in the melt later at lower temperature. By adding oligomers first the melt viscosity decreases very significantly, allowing the temperature to be lowered, and the lactide can then be mixed in at a lower temperature without significant volatilization. This is demonstrated in Example 16A.

Example 16A

A 90/10, L/D,L-lactide copolymer prepared by methods previously described, and analyzed by gel permeation chromatography to have a weight-average molecular weight of 480,000, a number average molecular weight of 208,000, was banded, that is, melted and mixed on an open 2-roll mill preheated to 350 F. The copolymer will not melt and band well on the mill below 350 F. To 25 grams of this melted copolymer was added 10 grams of oligomeric lactic acid of a degree of polymerization of 2.34. After all of the oligomeric lactic acid mixed in, the temperature was dropped to 300 F, where the mixing was still quite good. With the roll temperature at 300 F, 10 grams of L-lactide was added slowly and mixed. The mix was stripped from the roll and pressed into a thin film in a press at 300 F. The 5-10 mil thick film was colorless, transparent and very flexible. Without the lactide the resulting film would have been stiff. Without first adding the oligomeric lactic acid the lactide could not have been added on a mill without being lost to volatilization.

The blends of polylactide and lactide plasticizer are quite pliable, becoming increasingly so with increasing lactide content. They are colorless and transparent. Only a very faint (pleasant) odor of lactide is detectable and no discernable taste of lactide was noticeable. The Table 3 plasticized film samples were tear resistant, easily foldable, and can be punctured

without shattering or tearing. They stiffen somewhat when placed in a cooler (5 C, 40 F), but remain flexible and creasible without breaking. These films noticeably soften in the hand, indicating a glass transition temperature below 37 C. When the lactide content is less than 20 percent, the films will have a rattle typical of a polyolefin film. At greater lactide contents the films have the drape and "warm" feel of a plasticized poly(vinyl chloride) (PVC). In fact, the compositions of the invention are also a replacement for plasticized PVC in many applications.

As shown in Table 3, the elastic moduli (initial tangent moduli) can be relatively high, similar to a linear low density polyethylene (LLDPE). This is an indication of potential form stability. Lower moduli and tensile strengths are similar to low density polyethylene (LDPE). Physical properties, as a function of lactide content, were plotted as shown in Figures 1 and 2. Referring to Table 3, at approximately 17-20 percent lactide content, the tensile properties are similar to polyethylenes used in trash bags and shopping bags.

At lower lactide contents, the blends have a similarity to polypropylene. Some data can be compared in Table 3. Table 4 defines the conventional plastics used in the comparisons.

TABLE 3. TENSILE PROPERTY COMPARISONS OF PLASTICIZED PLA[(a)]

Ex. No.	Composition	Lactide % TGA	Elastic Modulus 1000 psi	1% Secant Modulus 1000 psi	Yield Strength 1000 psi	Strain at Yield %	Break Strength 1000 psi	Strain at Break %
5	90/10, L-/D,L-Lactide Copolymer	1.3	289	291	0	0	7.5	3
6	"	17.3	119	119	2.23	4	2.29	288
7	"	19.2	95.5	90.3	1.97	5	4.24	536
8	"	19.6	88.7	88.7	1.72	4	2.12	288
9	"	20.5	50.3	50.3	1.21	5	2.16	338
10	"	25.5	33.7	22.9	0.32	4	2.44	546

(a) ASTM 882; all samples were compression molded 5-10 mil films except Examples 13 and 14; strain rate 1.0 in/in min for all, D,L-lactide is racemic.

TABLE 3. TENSILE PROPERTY COMPARISONS OF PLASTICIZED PLA[a]
(Continued)

Ex. No.	Composition	Lactide % TGA	Elastic Modulus 1000 psi	1% Secant Modulus 1000 psi	Yield Strength 1000 psi	Strain at Yield %	Break Strength 1000 psi	Strain at Break %
11	LPDE[b]	--	41.3	40.6	1.51	17	1.60	365
12	LLPDE[c]	--	44.4	42.7	1.66	16	1.66	599
13	Biaxially[d] oriented PE	--	38.9	41.1	1.69	16	4.78	838
14	"[c]	--	35.6	38.5	1.68	16	5.20	940
15	HDPE[f]	--	127.8	120.9	3.48	9	1.95	216
16	pp[g]	--	174	174	5.08	5	7.34	6

(b) USI low-density polyethylene (petrothene No. 213)
(c) Exxon linear low-density polyethylene (LLPE 6202,57)
(d) Machine direction
(e) Cross machine direction
(f) Phillips high-density polyethylene (HMN 5060)
(g) Chisso polypropylene (XF 1932, melt index 0.52)

TABLE 4. MANUFACTURERS' DATA

Supplier	Trade Name and/or Grade	Density, gm/cu cm	Recommended Melt Temperature, F	Tensile Strength at Yield	Elastic Modulus in Flexure, 10^5 psi	Melt Index gm/10 min
LDPE (USI)	Petrothene No. 213	0.924	360-550	1820	0.37	8.0
LLDPE (Exxon)	6202.57	0.926	425	1700	0.53	12.0
HDPE (Phillips)	HMN 5060	0.950	425-525	3600	1.75	6.0
80% LLDPE (Exxon) 20% HDPE (Processing oil)	LPX 86 (Octene base)	0.927	260	--	--	0.8
Polypropylene (PP-Chisso)	XF1932	0.91	450-500	5872	3.05	0.52
Polystyrene (Amoco)	RI	1.05	400	7900	4.50	1.8

Table 3 reveals some data for lactide and polylactide mixtures. The results do not differ remarkably from similar compositions of Examples 1 and 2, prepared by other means. However, those skilled in the art will recognize that the precise physical properties will vary somewhat depending on the intimacy of the mixture, the tensile testing conditions, and the fabrication technique for preparing the films. Comparisons from Table 3 reveal that the lactide-polymer mixtures have a broad range of controllable compositions that mimic many conventional, nondegradable plastic types.

Example 17

An oligomeric poly(lactic acid) (OPLA) was prepared for mixing with polylactides as follows. An 88 percent solution of L-lactic acid (956 g) was charged to a 3-neck flask (1 liter) fitted with a mechanical stirrer and a pot thermometer. The reaction mixture was concentrated under a nitrogen purge at 150-190 C at 200 mm Hg for 1 hour until the theoretical water of dilution was removed. No catalyst was used except for lactic acid and its oligomers. This temperature and vacuum were maintained and distillation continued for 2 hours until 73 percent of the theoretical water of dehydration was removed.

The total time required was 3 hours. At this time the reaction was stopped. The water samples and the pot oligomer were titrated with 0.5N NaOH. Some lactic acid, 26.2 g, was found in the water distillate. The pot oligomer (OPLA) was also refluxed with excess 0.5N NaOH, then back titrated with standard H_2SO_4. The data are recorded in Table 5. The oligomeric poly(lactic acid) flows well when hot, and shows some cold flow. It has a degree of polymerization of 3.4. It was used in Example 20 where it was melt blended with the polymer of Example 19.

TABLE 5. CHARACTERIZATION OF OPLA OF EXAMPLE 1

Percent Dehydrated, Theoretical	Titratable Acid, percent	Titratable Ester, percent	Total Expressed as Lactic Acid percent	Degree of Polymerization
58	34.4	82.4	116.8	3.4

Example 18

The procedure of Example 17 was repeated except the distillation was conducted more slowly. After 8 hours of heating during which the temperature was slowly advanced from 63 to 175 C at 200 mm Hg, a sample of the pot was titrated to reveal 62.2 percent of theoretical water removal. Titration revealed a degree of polymerization of 4.3. The molecular weight of the oligomeric poly(lactic acid) was further advanced over 2 hours by heating at 179 C and using a vacuum pump. The oligomeric poly(lactic acid) was no longer soluble in 0.1N NaOH, was water white, and would cold flow. This material is a second example of an oligomeric poly(lactic acid) preparation with somewhat higher degree of polymerization as compared to Example 1. It was mixed with polylactide in Examples 22 and 25. It is estimated that the degree of polymerization was about 6-10.

Example 19

A polymer of lactide was prepared by methods similar to Example 3. A 90/10, weight percent L-/racemic D,L-lactide copolymer was melt polymerized using 0.02 parts per hundred, anhydrous stannous octoate catalyst. In a similar manner a 100 percent L-lactide homopolymer (L-PLA) was prepared. The copolymer was melt blended with the homopolymer at 350 F in a twin-screw extruder at a weight ratio of 90/10, copolymer/homopolymer. Gel permeation chromatography of the blend reveals a weight-

average molecular weight (M_w) of 182,000 and a number-average molecular weight (M_n) of 83,000. Residual lactide monomer by thermogravimetric analysis was 1.7 weight percent. This blend was mixed with the oligomeric poly(lactic acid) of Example 17 to provide material for Example 20. The tensile properties are listed in Table 6.

Example 20

The polymer of Example 19 was melt blended with the oligomeric poly(lactic acid) of Example 17 on an open, 2-roll, mill for 20 minutes at 325 F. The mix was compression molded into films and tested as shown in Table 6. The gel permeation chromatography molecular weights were smooth, monomodal distributions (M_w/M_n = 2.6) with M_w = 192,000 and M_n = 73,000.

TABLE 6. PROPERTIES OF MELT BLENDS OF 90/10 POLYLACTIDES AND OLIGOMERIC POLYLACTIC ACID

Example Number	Composition, wt.%		Lactide, %, TGA	Elastic Modulus, 1000 psi[a]	Break Strength, psi[a]	Strain at Break, %[a]	Tg, C[b]
	Polymer	Oligomer					
19	100[c]	0	1.7	298	7500	3	55
20	91[c]	9[d]	1.8	275	6113	2	--
21	100[e]	0	1.6	308	7478	3	58
22	70[e]	30[f]	0.4	254	5052	3	42
23	60[e]	40[f]	0.0	202	3311	2	38
24	50[e]	50[f]	0.0	106	2334	25	35
25	40[e]	60[f]	0.0	36	1180	129	35

(a) ASTM 882; 5-10 mil, compression-molded films; strain rate 1.0 in./in./min.
(b) Glass transition temperature by differential scanning calorimetry
(c) A blend of 90% of a 90/10, L-/D,L-lactide (racemic) copolymer with 10% poly(L-lactide), Example 19.
(d) Oligomeric PLA of Example 17
(e) A blend of 80% of a 90/10, L-/D,L-lactide (racemic) copolymer with 20% poly(L-lactide)
(f) Oligomeric PLA of Example 18

Example 21-25

The copolymer of Example 19 was melt blended with 20 percent of the L-PLA described in Example 19. The blend is listed as Example 21 in Table 6, where its analyses and tensile properties are listed. Example 21 was, in turn, melt blended with various amounts of the oligomeric poly(lactic acid) of Example 18 and these were tested as before and listed in Table 6, Examples 22 to 25. Table 7 lists the gel permeation chromatography molecular weights of these compositions. The tensile strengths and moduli are compared to the weight percentages of oligomeric poly(lactic acid) in Figures 3 and 4 (Lower Curves).

TABLE 7. MOLECULAR WEIGHTS AND GLASS TRANSITION TEMPERATURES OF 90/10 POLYLACTIDES AND OLIGOMERIC POLYLACTIC ACID

Example Number	Composition, wt.%		Res.[a] Mon., %	GPC x 10^{-3}[b]			M_w/M_n	Tg[c], C
	Copolymer	Oligomer		M_n	M_w	M_z		
21	100[d]	0	1.6	76	175	410	2.3	58
22	70[e]	30[f]	0.4	67[g]	136	299	2.0	42
23	60[e]	40[f]	0.0	61[g]	112	211	1.8	38
24	50[e]	50[f]	0.0	62[g]	114	223	1.8	35
25	40[e]	60[f]	0.0	69[g]	120	207	1.7	35

(a) Residual monomer by TGA
(b) Molecular weight by GPC
(c) Glass transition temperature by DSC
(d) A blend of 90% of 90/10, L-/racemic D,L-lactide copolymer with 10% L-Pla
(e) Example 21
(f) Example 18
(g) After blending; melt-blending on an open mill roll at 325 F.

All D,L-lactide is racemic, not meso.

Examples 26-30

A second series of copolymers was blended with the oligomeric poly(lactic acid). A 92.5/7.5, L-/racemic D, L-lactide copolymer was prepared by methods similar to Examples 19 and 21. This is Example 26 of Tables 8 and 9. It was melt blended with the oligomeric poly(lactic acid) of Example 18 on an open, 2-roll mill at 325 F for approximately 20 minutes. The blends were compression molded into 3-5 mil thick films and their tensile properties and gel permeation chromatography molecular weights measured. The properties are recorded in Tables 8 and 9, and plotted in Figures 3 and 4. The second series of blends revealed significantly higher values for the tensile properties although the molecular weights were lower. This may be due to lower residual lactide monomer and/or the change in high polymer composition. All of the oligomeric poly(lactic acid) polylactide blends could be easily molded into tack free, transparent films.

TABLE 8. PROPERTIES OF MELT BLENDS OF 92.5/7.5 POLYLACTIDES AND OLIGOMERIC POLYLACTIC ACID

Example Number	Composition, wt.%		Lactide, %, TGA	Elastic Modulus, 1000 psi[a]	Break Strength, psi[a]	Strain at Break, %[a]	Tg[b], C
	Polymer[c]	Oligomer[d]					
26	100	0	0.2	338	10,527	4	61
27	80	20	0.3	346	9,144	4	52
28	70	30	0.2	346	5,675	2	46
29	60	40	0.6	249	5,617	3	36
30	50	50	1.5	112	1,984	119	36

(a) ASTM 882; 3-5 mil, compression-molded films; strain rate 1.0 in./in./min.
(b) Glass transition temperature by differential scanning calorimetry
(c) 92.5/7.5, L-/racemic D,L-lactide copolymer
(d) Example 18

All D,L-lactide is racemic, not meso.

TABLE 9. MOLECULAR WEIGHTS OF 9.25/7.5, L-/RACEMIC D,L-LACTIDE COPOLYMERS

Example No.	% OPLA	GPC x 10^{-3} [a]			M_w/M_n
		M_n	M_w	M_z	
26	0	63	124	228	1.95
27	20	60	108	189	1.81
28	30	48	80	125	1.66
29	40	59	96	151	1.65
30	50	56	92	141	1.64

[a] Gel permeation chromatography (GPC) molecular weights as referred to monodisperse polystyrene standards

Examples 31 and 32

Film specimens with, and without plasticizer were exposed to seawater at Daytona, Florida from March through May. The pH of the water varied from 7.3 to 7.6 and the salinity from 33.2 to 38.4 ppt. The water gradually warmed in the test from 15 to 27 C. The specimens were cut into strips and tensile tested before, and after, periodic intervals in the seawater. The results are shown in Table 10. All of the samples showed whitening and physical degradation, which became progressive with time. Without plasticizer the samples showed whitening and degradation after six weeks in the seawater. The oligomeric poly(lactic acid) polylactide blend degraded faster, revealing clear evidence of degradation after 3 weeks. The incorporation of 20 percent lactide provoked immediate whitening and obvious degradation after one week of exposure.

TABLE 10. PHYSICAL PROPERTIES AFTER SEAWATER EXPOSURE

Example Number	Composition	Seawater Exposure Weeks	Tensile Properties, 1000 psi[a]				Strain, %	
			Elastic Modulus	1% Secant Modulus	Yield Strength	Break Strength	Yield	Break
31	90/10 copolymer 5% L-PLA	0	305	292	--	7.6	--	4.7
		3[b]	315	301	--	7.1	--	3.1
		6[c]	317	317	--	7.3	--	3.0
		9[d]	228	230	--	6.2	--	3.0
		12[e]	355	343	--	3.9	--	1.0
20	90/10 copolymer with 10% oligomer	0	275	275	--	6.1	--	2.0
		3[b]	291	281	--	6.8	--	2.9
		6[c]	246	246	--	3.9	--	2.0
		9[d]	211	105	2.2	1.4	3	2.0
		12[e]	103	103	--	1.7	--	1.0
32	90/10 copolymer with 1% fumaric acid	0	300	298	--	7.0	--	3.0
		3[b]	292	291	--	6.5	--	2.5
		6[c]	318	318	--	6.9	--	2.0
		9[d]	226	223	--	6.1	--	3.0
		12[e]	70	122	--	0.8	--	1.0
9	92.5/7.5 copolymer with 20% lactide	1[e]	- - - - - - - - Too brittle to test - - - - - - - -					

(a) 0.5 x 5 in. strips of film, 12-17 mil; strain rate 1 in./in./min.
(b) 15-21 C, saline seawater, regularly exchanged
(c) 20-22 C, saline seawater, regularly exchanged
(d) 22-23 C, saline seawater, regularly exchanged
(e) 22-27 C, saline seawater, regularly exchanged

Example 33

Examples 33 to 51 teach the use of incorporating lactide in conjunction with quenching to obtain pliability and transparency. Alternatively, the polymers can be annealed to improve stability against heat distortion.

Poly L-(lactide) was prepared by methods previously described. Thus 300 g of triply recrystallized and thoroughly dried L-lactide was loaded into a clean, flame-dried, argon-cooled, 500 ml round-bottom flask. The flask was fitted with a rubber septum and inlet and outlet syringe needles that admitted a continuous argon purge. Stannous octoate solution was prepared by dissolving 20 g in 110 ml of toluene, previously dried over molecular sieves, then distilling 10 ml toluene in order to azeotropically dry the solution. The final concentration was 0.2 g/ml stannous octoate in toluene. A 0.3 ml quantity was injected through the septum onto the L-lactide. The flask and its contents were placed in a 150 C oil bath, and when melted, swirled vigorously to obtain a homogeneous mix. The argon purge continued and a thermocouple was fitted through the septum into the melt. The melt was 143 C. The temperature of the oil bath was advanced to 200 C and heating and light purge continued for 20 hours. The temperature of the melt advances to 170-174 C in the first two hours of heating. The final temperature was 170 C. After 20 hours of heating the flask was cooled in air to room temperature and the solid polymer was transparent.

Polymer was recovered by shocking the flask with dry ice to free it from the glass. The residual monomer was analyzed by thermogravimetric analysis and the molecular weights by gel permeation chromatography. Differential scanning calorimetry reveals a glass transition temperature (T_g) at 53 degrees and two melting point endotherms with peaks at approximately 170 and 190 C. The gel permeation chromatography molecular weights: M_n = 129,000; M_w = 268,000; M_z = 462,000; M_w/M_n = 2.08.

Residual monomer by thermogravimetric analysis was 2.3 percent, (Example 33, Table 11.) The experiment shows that L-lactide can be polymerized above, or near, its melting point and the products remain transparent and more amorphous.

Example 34

By methods similar to Example 33, 104.0 g of L-lactide was polymerized using 0.10 ml of stannous octoate catalyst solution. However, the reaction temperatures were 155-165 C for 72 hours. The polymer (No. 34 of Table 11) slowly crystallizes upon forming and is a white opaque solid at reaction or room temperature. Since the sample was smaller than the preceding experiment the polymer cooled more quickly, but it did still not quench to a transparent solid. In comparison to Example 33, the lower reaction temperature permits the poly(L-lactide) to crystallize and become opaque, thus an intimate dispersion of plasticizer does not form.

The temperature is slowly advanced in many of these experiments to accommodate the polymerization exotherm. The reaction temperature must reach at least 170-175 degrees before there is substantial monomer-to-polymer conversion, otherwise the poly(L-lactide) crystallizes and is difficult to remelt.

In Examples 36-42 the polymerization of L-lactide was repeated varying the conditions to obtain poly(L-lactides) with different residual lactide contents and crystallinities. The results are shown in Table 11, where it is seen that pliability and toughness were obtained only when the product has been quenched from the melt, is transparent at room temperature, and contained approximately 10 percent or more residual lactide. It is believed that the L-lactide homopolymer must be polymerized in the melt, and quenched from the monomer-polymer melt temperatures, to a transparent material as evidence of its homogeneous and intimately plasticized

properties. When the poly(L-lactide) crystallizes during polymerization because the polymerization temperature is well below the polymer's melting point, the residual monomer is no longer effective as a plasticizer. If the polymer crystallizes upon cooling to room temperature, it also loses its plasticization. Annealing at elevated temperatures will restore crystallinity to amorphous samples.

TABLE 11. POLYMERIZATION OF L-LACTIDE

Ex. No.	Catalyst Amount pph	Temp C	Time Hours	Polymer Appearance	Residual Monomer Percent	Sample Size g
33	0.02	156-201[a] 150-174[b]	20	clear transparent, hard, glassy	2.30	300
34	0.02	155-165[a]	72	crystalline, opaque, hard, brittle	--	104
35	0.005	120-200[a] 111-200[b]	24	crystalline, opaque, hard, brittle	--	100
36	0.02	135-145[a] 135-152[b]	22	crystalline[d], opaque, hard, brittle	1.1	500
37	0.02	117-185[a] 120-175[b,c]	24	crystalline, opaque, hard, brittle	1.74	100
38	0.02	160-170[a]	8	crystalline, opaque, hard, brittle	2.18	2,000
39	0.02	145[a] 137-144[b]	15	crystalline, opaque, hard, brittle	3.6	25
40	0.0553	190[a] 160-215[b]	0.3	clear, pliable, tough, transparent	10.1	25
41	0.0553	188-193[a] 147-200[b]	0.28	clear, transparent, pliable except at edge of polymerizate	22.9	25
42	0.02	145[a] 150-133[b]	2.75	crystalline[d], opaque, hard, brittle	52.5	25

(a) Oil bath temperature
(b) Polymer melt temperature
(c) This polymer crystallized at 160-169 as the temperature was advanced, and it did not remelt.
(d) Transparent at reaction temperature; crystallizes upon cooling.

This transparency and intimacy of association between polymer and monomer is also affected by the ratio of L/D,L-lactide. At approximately 95/5 ratio the copolymer easily quenches to a transparent solid. The 90/10 ratio, L/D,L-lactide copolymer quenches quite

easily. The 100 percent L-lactide polymer quenches with difficulty from thick sections of the polymer to a transparent material. Some comparisons are shown by Examples 43-47 of Table 12. Thinner cross sections, i.e., films of the L-lactide polymer can be plasticized and quenched to pliable and transparent materials. The 80/20 copolymer quenches very easily to a transparent solid. The latter has only a trace of crystallinity as seen by differential scanning calorimetry.

TABLE 12. TRANSPARENCY OF LACTIDE POLYMERS

Ex. No.	Lactide L/D,L-Ratio	Temp., C[a]	Time, Hours	O/T[b]	GPC M_w	Residual Monomer, percent
43	95/5	145-160	67	SO	385,000	2.64
44	100	135-152	22	O	322,000	1.1
45	90/10	150-157	45	T	821,000	4.95
46	90/10	150-170	48	T	278,000	1.37
47	80/20	135-175[c]	23	T	--	--

(a) Melt temperature (polymerization temperature)
(b) Opaqueness/transparency (O/T) after air-cooling of polymerizates; opaque (O); slightly opaque (SO); transparent (T)
(c) Slow-cooled for 1 hour

All D,L-lactide is racemic.

All of the lactide polymers thermoform easily, that is, when heated by a radiant heater until soft, then sucked down on an intricate mold, they all forr the pattern of the mold easily. However, the poly(L-la e) becomes partially cloudy and hazy upon cooling. The /5, 90/10, and 80/20 copolymers are quite clear and transparent throughout their thermoforms.

Example 48

The poly(L-lactide) from Example 33 was melted and mixed on an open 2-roll mill for 5 minutes at 375 F

(190 C), then compression molded at 375 C for 2 minutes, then air-quenched to room temperature in approximately 30 seconds. Both 7-and 20-mil thick films were prepared. Both were clear and transparent without trace of haze or opacity. Residual monomer in the film was 0.79 percent. The films are very stiff.

Example 49

The experiment was repeated except that the milling was continued for 10 minutes instead of 5 minutes. The films were analyzed by thermogravimetric analysis again and found to have 0.38 percent lactide. The films were clear, transparent, and stiff.

Example 50

The mill-rolled polymer was also compression molded into a 1/4 x 1/2 x 1 inch plaque. This plaque required 5-10 minutes to cool in the press by turning on the cooling water to the press. The plaque was white, opaque, and crystalline except for the extreme edges, which were transparent.

The above Examples 48-50 teach the quenching of films of poly L-lactide to maintain transparency. When cooled more slowly, they crystallize and lose their transparency.

As D,L-lactide is introduced as a comonomer, quenching can be replaced by ordinary cooling to retain transparency. Spherulitic crystallinity can be introduced into these films by annealing and the 100 percent L-lactide polymer is the fastest to crystallize. Where transparency is not required the higher L-lactide polymers can be annealed to greatly improve their resistance to thermal distortion. Conversely, where transparency is required, such as in a polystyrene offset, great care must be taken to avoid this type of opaque crystallinity.

Example 51

The poly(L-lactide) film samples were annealed on a hot plate at 240 F (115 C). The film turned hazy in approximately 1 minute and completely cloudy in approximately 2 minutes. By way of comparison, a 90/10, L/D,L-lactide copolymer film required 10 minutes to turn hazy, 15 minutes to become completely cloudy. When suspended by one end horizontally in an oven and advancing the temperature slowly, the annealed poly(L-lactide) sample remained straight until a temperature of 295 F (146 C) was obtained. The film then bent over. The annealed 90/10 copolymer bent over at a temperature of 185 F (85 C). The results show that the amount of crystallinity of polylactides can increase their form-stability at elevated temperatures to a temperature that is well above their T_g.

Examples 52-55

The following examples illustrate the beneficial effects of adding lactide during compounding. The examples show that without lactide as modifier, the lactide polymer degrades during compounding. With the addition of lactide both discoloration and molecular weight decrease are prevented or substantially reduced during compounding.

Thus, in Example 52, a 90/10, L-/D,L-lactide copolymer prepared as described by previous methods using 0.02 pph $SnCl_2 \cdot 2H_2O$ catalyst was ground and extruded into pellets from a twin screw compounder, adding 5 weight percent lactide. The melt zone temperature of the extruder rose to 390 F, the polymer discolored, and the weight average molecular weight (M_w, by gel permeation chromatography) decreased by approximately 40 percent. The results indicated that insufficient lactide was added for this very high M_w copolymer. The results are shown in Table 13. The pellets from this compounding were recompounded adding a further 10 weight percent lactide (Example 54). The melt zone temperature was 375 F, and

the results were much better: further discoloration did not occur, molecular weight decreased slightly, or within experimental error, and a pliable composition was obtained.

TABLE 13. EFFECT OF LACTIDE AS MODIFIER DURING COMPOUNDING

Ex. No.	Before Compounding Color	M_w [a]	M_w/M_n [a]	Lactide[b] weight percent
52	Light yellow	513	2.15	0.78
53	Light yellow	278	1.80	1.37

Ex. No.	After Compounding Color	M_w [a]	M_w/M_n [a]	Lactide[b] weight percent
52	Dark yellow	322	2.05	5.56[c]
53	Yellow	184	1.90	2.26
54	Dark yellow	307	2.00	14.4[d]
55	Colorless[e]	324	1.99	14.6

(a) GPC x 10^{-3}
(b) By thermogravimetric analysis, at 200 C
(c) Five weight percent lactide added during compounding.
(d) Further 10 weight percent lactide added during compound.
(e) Thin film

To ascertain that the second compounding and extrusion were facilitated due to the lactide modifier and not the decreased molecular weight, another compounding (Example 53) was performed starting with a similar-M_w copolymer of 90/10, L-/D,L-lactide. In this case, no lactide was added back in during the compounding. The melt zone temperature was 382 F, the copolymer was discolored, and the M_w decreased by approximately 66 percent. In addition, approximately 5 percent more torque was required to compound the mix of M_w 278,000 as compared to the one of M_w of 322,000 with added lactide.

After compounding twice with lactide, Example 54 was analyzed by thermogravimetric analysis and found to have a lactide content of 14.4 percent. The material of Example 54 was converted to a blown film by means of a Haake-Brabender extruder in Example 55. Thin films of this composition are colorless, highly transparent, and very pliable and extensible as described below in Examples 60 - 64. The Mw by gel permeation chromatography was 324,000 (cf. Mw = 307,000 before compounding and extrusion). The Tg of this plasticized material is 42 C and differential scanning calorimetry reveals a very small amount of crystallinity melting at approximately 138 C. The amount of lactide present is 14.6 percent as estimated by thermogravimetric analysis.

Examples 56 and 57

The compounded polylactides, Example 52 and 53, were mixed together in the twin-screw compounder with extra lactide to raise the lactide level to approximately 20 percent. The compounding temperature was 347 F (175 C), much reduced from the previous 375 to 385 F. The compounding proceeded smoothly without further discoloration.

The above results clearly show the beneficial effects of added lactide as modifier. The required torque to compound the compositions, the discoloration, and the working temperature are decreased when adding lactide. Further evidence of plasticization is seen in the lowered Tg and the pliability of the compositions. In addition, molecular weight decreases are avoided and stable compositions are obtained. It will be obvious to those skilled in the art that the amount of lactide employed depends on many factors, including the desired amount of plasticization sought, the type of compounder that is used, and the molecular weight of the polylactides.

Examples 58 and 59

Examples 58 and 59 illustrate blown film extrusion of polylactides. These pliable films mimic polyolefins. The plasticized compounds of Examples 56 and 57 were adjusted to approximately 20 percent lactide in the twin-screw extruder. They were converted to blown films using a Haake-Brabender extruder. This consists of a 3/4-inch extruder with a blown-film die and take-up device. The blown-film was achieved using a 12.7 mm outside diameter orifice and a pin to establish an extrusion gap of 0.483 mm. An extrudate temperature of 187 C was maintained. A stable bubble was blown at this temperature with the inflation air at 3 oz/in.^{2} gauge pressure. Cooling air was blown against the exterior of the bubble at 18 psi. Since the final average film thickness was 0.158 mm (6.2 mil), the blow-up ratio was 3:1. When the extruder gap was reduced from 0.483 to 0.254 mm, or the temperature raised, the polymer quenched readily to a crystalline, cloudy extrudate that would not expand. The larger orifice die produced an extrudate that was thicker and more viscous, cooled more slowly, and expanded in a consistent manner. The extruded film exhibited some elastic memory when stretched. The film also was resistant to tear and puncture and was very difficult to break by stretching. The blown film had an average elastic modulus of 117,000 psi, an average tensile strength of 3,735 psi, and an average elongation to break of 370 percent. This modulus is slightly higher than that of linear low density polyethylene, but the strength and elongation to break are comparable. The Elmerdorf Tear Strength (ASTM 1922) was 424 g in the cross machine direction and 183 g in the machine direction. The Tg of the material was 36 C, Mw by gel permeation chromatography was 229,000, the residual lactide by thermogravimetric analysis was 19.7 percent, and the differential scanning calorimetry curves showed a weak endotherm centered at approximately 135 C.

Examples 60-64

These examples illustrate plasticization with oligomeric esters of poly(lactic acid). Copolymers of 90/10, L-/D,L-lactide were melt blended with added lactide, esters of oligomeric/lactic acid, and mixtures thereof. They were characterized by tensile and thermal properties.

In Example 60, a control copolymer of 90/10, L-/D,L-lactide was assayed by thermogravimetric analysis to be 6.74 percent lactide. This was mixed with 30 percent by weight oligomeric polymethyllactate (Mella) in Example 61, which was prepared by heating 2,500 g of (S)-methyllactate in an autoclave at 210 C for 3 hours, then collecting the Mella which fractionally distilled at 81 to 85 C/1.25 torr. The mixture was melt blended on an open 2-roll mill at approximately 350 F. The blend was compression molded in a press at approximately 350 F into clear, pliable films. The tensile properties, before and after, adding the Mella are recorded in Table 14. The glass transition temperature (Tg) was reduced by the Mella plasticizer.

For Example 62, the 90/10, L-/D,L-lactide copolymer was melt blended with added L-lactide in a twin screw extruder to adjust the L-lactide content to 20 percent by weight. The blend was further mixed with oligomeric polyethyllactate (Ella) (Example 63) and Mella (Example 64). The properties of these blends are also recorded in Table 14.

TABLE 14. CHARACTERISTICS OF POLYLACTIDES[a] PLASTICIZED WITH OLIGOMERIC ESTERS OF LACTIC ACID

Ex. No.	Plasticizer	Elastic Modulus psi	Break Strength psi	Strain at Break, %	T_g[b]	T_m[c]
60	6.74%[d] L-lactide	370,000	6,903	2	51	141
61	6.74%[d] L-lactide and 30% Mella[e]	154,000	2,012	100	30	141
62	20% L-lactide	101,000	2,637	278	--	--
63	20% L-lactide and 30% Ella[f]	7,316	2,561	339	--	--
64	20% L-lactide and 30% Mella[e]	3,620	495	83	--	--

[a] 90/10, L-/racemic D,L-lactide copolymer
[b] Glass transition temperature
[c] Melting point
[d] Analyzed by thermogravimetric analysis
[e] Methyllactate oligomer
[f] Ethyllactate oligomer

Examples 65-81

Comparative Examples 65 to 81 were selected from the patent literature that presented conditions most likely to result in materials of the present invention. The materials produced in these patents were not completely characterized, thus experiments were needed to allow a more complete characterization of the examples and provide meaningful comparisons that would demonstrate that the materials of the present invention are indeed novel. With regard to the present invention, compositions were sought that had residual lactide or lactic acid contents of about 0.1 to about 60 weight percent and in addition may have the lactide or lactic acid intimately dispersed within the polymer. The results fall into obvious categories. Thus, products with number-average molecular weights, M_n, less than 10,800 do not have the physical properties required in the present invention. In fact films from these low M_n compositions were too brittle to be handled for tensile measurements.

It is known from the teachings herein that lactic acid, lactide, or oligomers of lactide or lactic acid, or derivatives of lactic acid must be, present to provide plasticization and some pliability. The lactide must be present in amounts greater than about 10 weight percent while the oligomers of lactic acid, oligomers of lactide and the derivatives of lactic acid must generally be present above about 40 percent to provide obvious plasticization and pliability to polylactides. However, any amount of plasticizer as taught herein when added to the composition will change properties and can be used to obtain specialty formulated compositions. Thus, if lactide is intimately dispersed and effectively mixed as plasticizer, the mix of lactide and polylactide is completely transparent. The heterogeneous domain size of the lactide is small enough, generally less than one micron, so that it will no longer scatter light, i.e., it is intimately dispersed. Conversely, white opaque samples are always hard because they have crystallized under the test conditions. Crystallization squeezes the lactide out of the polymer mass, resulting in hard stiff compositions that are a gross mixture of monomer and polymer. This is also obvious from differential scanning calorimetry (DCS). Monomeric lactide that has segregated reveals itself with a separate melting point at 95 to 100 C, whereas well-plasticized samples do not show a distinct monomer melting point.

One very important point is that the cited patents frequently specify L-lactide homopolymer ("100 percent L-" in Tables 15A and 15B). The homopolymer of L-lactide easily crystallizes because of its high melting point. At lower reaction temperatures, the homopolymer can retain appreciable quantities of monomer, but the composition freezes during polymerization. At higher reaction temperatures, the L-lactide polymerizes so quickly that it is very difficult to stop the

polymerization with substantial monomer left in the product.

Inspecting the results listed in Table 15A and 15B reveals that the comparative examples obtain either products with low residual lactide or else the polymerizations did not work or worked so poorly that greater than 40 percent lactide was left at the end of the specified polymerizations. Thus, Examples 65, 66 (very similar also to the work of Schneider), 67, 69, 73, 74, and 75 obtain low residual lactide. The Examples 70, 71, 72, 76, 77, and 78 examples did not work well as written in the patent examples. The best known laboratory techniques were added to the procedures, described in the footnotes, on these examples, from a historical standpoint (monomer purity, for example) in an effort to make the procedures work, with indifferent success. In no examples were pliable products found. Either glassy, or hard, crystalline, opaque products were obtained. It should be noted that only those examples using tin compounds as catalysts appear to be acceptable for many packaging applications.

It appeared particularly that the Tunc methods would provide the materials of the present invention. To ascertain this, it was necessary to do the listed experiments on the teachings of Tunc in laborious detail as shown in Examples 79 to 81. Figure 5 is a differential scanning calorimetry of one of the polylactides of the present invention. There is no detectable melting point for residual lactide monomer in the vicinity of 95 to 100 C. Only the polymer melting is seen. This material was analyzed separately by thermogravimetric analysis and shown to be 18.4 percent monomer lactide.

By way of contrast, preparations according to the exact replication of the Tunc methods were performed. Thermogravimetric analysis reveals 20.2 percent residual lactide for one such preparation, Example 80. The differential scanning calorimetry of this material is

shown in Figure 6, where a very distinct monomer melting point is seen. This corresponds to segregated lactide with a melting point within its own heterogeneous domain. Whereas this polymer is white, opaque, very hard and stiff, the composition of the present invention preparation is clear, transparent, and very pliable.

A similar result was obtained repeating the teachings of Tunc in Example 81. This analyzed as 32.2 percent lactide and revealed a monomer melting point (Figure 7). The material was very white, crystalline, and hard. The results are reviewed in Table 15A and 15B.

TABLE 15A. RELATED ART POLYMERIZATIONS OF LACTIDE CONDITIONS

Ex. No.	Patent	Pat. Ex.	Lactide Monomer (s)	Catalyst		Polymerization	
				Type	pph	Temp. C	Hours
65	2,758,987	1	L-	PbO	0.30	150	42
66	2,758,987	3	50/50 L-/D,L	PbO	3.00	150	89
67	3,982,543	3	L-	PbO	0.30	150	31
68	DD 14548	2	L-	SnO[a]	0.009	193	3
69	4,137,921	4	90/10 L-/D,L	$Sn(Oct)_2$, GA/ dioxane[b]	0.0553	180 190 210	0.33 0.33 0.33
70	GB 755,447	4	D,L	ZnO[c]	0.02	150	24
71	GB 755,447	2	D,L	Zn Powder[d]	0.02	140	25.5
72	GB 755,447	6	D,L	Zn Carbonate Hydroxide[c]	0.02	140 150	2 3
73	CA 932,382	1	D,L	Tetraphenyl Tin	0.02	165	20
74	CA 923,245	1,7 & 8	L-	Et_2Zn	0.167	105-110	2
75	DE 946,664	2	D,L[e]	$ZnCl_2$	0.25	140	48
76	DE 1,112,293	1	L-	Sn Stearate	0.0087 as Sn	205-210	0.5
77	2,951,828	1	L-[f]	$SnCl_4$ suspension[g]	0.30	160	5
78	3,268,487	2	D,L	Tris(2-chloroethyl)amine[h]	0.88	80	24
79	EP App. 108,635 (1984); 4,550,449; 4,539,981	6, Polymer 8	L-	$Sn(Oct)_2$	0.00108	165	93
80	4,539,981; 4,550,449	Polymer 33	L-	$Sn(Oct)_2$	0.00119	136-139	64
81	4,539,981; 4,550,449	Polymer 37	L-	$Sn(Oct)_2$	0.00324	115	64.5

[a] No reaction until recipe was changed by adding 0.75 pph of 88 percent lactic acid. Product was white, opaque, very hard and brittle; film too brittle to handle.

[b] Included was glycolic acid as chain transfer agent.
[c] Insoluble
[d] Insoluble after 24 hours plus additional 1.5 hours with 700 μl 88 percent lactic acid and 100 μl H_2O.
[e] In toluene; product colorless and very viscous.
[f] In mineral spirits, Stoddard solvent No. R-66.
[g] Agglomerated
[h] In dioxane containing 0.517 pph KOH; no polymerization.

TABLE 15B. RELATED ART POLYMERIZATIONS OF LACTIDE RESULTS

Ex. No.	Residual Monomer, Percent	GPC x 10^{-3} M_n	M_w	M_z	M_w/M_n	Polymerizate Appearance
65	0	254	454	717	1.79	Light yellow, crystalline, opaque
66	0	97	187	322	1.94	Light yellow, transparent
67	0.85	95	195	325	2.06	Partially opaque crystalline, partial transparent
68	17.5(a) 7.1; 7.7	5 7	7 8	9 10	1.47 1.25	White, crystalline, opaque
69	4.6	116	218	356	1.88	Light yellow, transparent
70	47.7	--	--	--	--	White, crystalline (monomer), opaque
71	65.3	--	--	--	--	White, crystalline (monomer), opaque
72	79.6	--	--	--	--	White, crystalline (monomer), opaque
73	1.4	116	214	340	1.84	Yellow, transparent
74	1.9	80	150	235	1.87	Orange, crystalline, opaque
75	5.4[i] 2.5; 1.9[j]	164 307	377 527	657 808	2.3 1.72	Hard, colorless
76	43.3	30	35	41	1.17	Hard, crystalline, opaque
77	8.6; 9.6	219	343	504	1.57	Hard, crystalline, opaque
78	100	--	--	--	--	All crystalline monomer
79	5.0 film[k]	14 14	26 26	35 35	1.88 1.82	White, crystalline, opaque Some transparency at edges
80	20.2[l]	Greater than 1,000,000				White, crystalline, opaque
81	32.2[m]	Greater than 1,000,000				White, crystalline, opaque

(i) Sample heated at 140 C, then 5 minutes in 60 C vacuum oven to remove solvent.
(j) Sample heated overnight in 60 C vacuum oven to remove solvent.
(k) Transparent, very stiff and brittle.
(l) Tunc obtains 17.1 percent, very high molecular weight.
(m) Tunc obtains 28.0 percent, very high molecular weight.

The above examples establish that an all-lactic acid composition can be a pliable thermoplastic useful for flexible, plastic packaging films and containers. By way of comparison, nonplasticized homopoly (L-lactide) is a highly crystalline polymer with a tensile strength of about 7000 psi with an elongation of 1 percent and an initial modulus of 500,000 psi. It is very brittle, opaque, and crazes easily. It is not a well behaved thermoplastic, nor is it transparent. Poly (racemic D,L-lactide) is an amorphous, glassy, polymer with a glass transition temperature of approximately 50 C, a tensile strength of about 6300 psi, an elongation of approximately 12 percent, and an initial modulus of 160,000 psi. It is also very brittle although transparent. In stark contrast, a copolymer of L-lactide/racemic D,L-lactide that is plasticized with lactide monomer is remarkably different. For example, the plasticized polymers can have a tensile strength of approximately 3900 psi, an elongation of 431 percent, and an initial modulus of 56,000 psi. The plasticized polymer is clear and colorless, and the blend must be heated to above 100 C to remove the plasticizer.

Although theory would predict a more amorphous structure as a result of plasticization, what is surprising is the pliable, transparent, stable compositions that can arise, and, secondly, the nearly exact fit of properties needed for certain packaging applications, such as polyethylene. This invention comes at a time when there is a need for such initial properties in a material that is slowly environmentally biodegradable since it could alleviate plastic pollution problems.

It will be apparent to those skilled in the art that extremely intimate blends of high polymers and plasticizers are a rarity. Intimate plasticization allows a wide latitude in the initial physical properties and the time for environmental biodegradation.

The amount of plasticizer in the polymer depends on the compositional characteristics desired. If lactide is used as plasticizer the range is preferably 10 to 40 weight percent whereas if only oligomers of lactide or lactic acid are used the range may be from 10 to 60 weight percent. Surprisingly, oligomer may be added at up to 30 weight percent without substantially affecting the tensile strength or modulus. See Figures 3 and 4. Addition of 30 to 60 weight percent oligomers produces significant plasticization and attenuation of physical properties. This adds great economy to the composition since oligomeric lactic acid is cheaper than the high molecular weight polylactide. Oligomer may be prepared from lactic acid or any lactide. It is important to note that the oligomer of lactic acid normally contains significant amounts of lactic acid unless removed. This is an important consideration in tailoring compositions having specific properties. Those skilled in the art and knowing the teachings of this invention will be able to select reaction conditions to obtain appropriate chain lengths for the polymer, and the proportions of polymer and plasticizer so as to obtain fabricated compositions having physical properties similar to commonly used packaging thermoplastics and yet degrade comparatively rapidly. For example, higher amounts of plasticizer result in polymers having increased flexibility and increasingly tough physical properties, however, an increasing degradation rate will also be obtained. Further, shorter chain lengths for the polymer will require less plasticizer to obtain the same properties as with longer lengths.

Preferably polymerization of the monomers is at a temperature less than 129 C. Further processing of the plasticized polymer into a final product is preferably at a temperature sufficiently low to retain the plasticizer in the polymer. This temperature may be above 129 C. If additional monomer and/or oligomer are added after

polymerization the retention of monomer during processing is of course not as critical.

The unoriented compositions of the invention should have a tensile strength of 300 to 20,000 psi, an elongation to failure of 50 to 1,000 percent and a tangent modulus of 20,000 to 250,000 psi. Preferably for a polyolefin replacement the compositions have a tensile strength of at least 3000 psi, an elongation to failure of at least 250 percent, and a tangent modulus of at least 50,000 psi.

A composition for the replacement of polyethylene is adjusted so that the unoriented composition has a tensile strength of about 1,200 to about 4,000 psi, an elongation to failure of about 100 to about 800 percent, and a tangent modulus of about 20,000 to about 75,000 psi, while a composition for the replacement polypropylene, is adjusted so that the unoriented composition has a tensile strength of about 4,500 to about 10,000 psi, an elongation to failure of about 100 to about 600 percent, a tangent modulus of about 165,000 to about 225,000, and a melting point of about 150 to about 190 F.

The homopolymers and copolymers of the present invention are insoluble in water but upon constant contact with water are slowly degradable. However, degradation is fast when compared to polyolefin compositions that are replaced by the invention. Thus, throwaway objects made from the polymers are environmentally attractive in that they slowly degrade to harmless substances. If objects made from polymers of the invention are incinerated, they burn with a clean, blue flame.

The compositions herein are useful for replacement of polyolefin compositions and particularly polyethylene and polypropylene as well as polyvinyl chlorides and polyethylene terephthalate. In addition to the above list, the method is useful for replacement of polymers of styrene, vinyl acetate, alkyl methacrylate, alkyl acrylate. It is understood that copolymers made

from mixtures of the monomers in the listed group and physical mixtures of the polymers and copolymers of the above group are likewise replaceable. Those skilled in the art will recognize that minor amounts of lactide and lactic acid can be replaced by contemplated equivalents such as glycolide, glycolic acid, and caprolactone.

B. Second General Embodiment

The environmentally degradable compositions disclosed herein are completely degradable to environmentally acceptable and compatible materials. The intermediate products of the degradation: lactic acid is a widely distributed naturally occurring substance that is easily metabolized by a wide variety of organisms. Its natural end degradation products are carbon dioxide and water. Contemplated equivalents of these compositions such as those that contain minor amounts of other materials, fillers, or extenders can also be completely environmentally degradable by proper choice of materials. The compositions herein provide environmentally acceptable materials because their physical deterioration and degradation is much more rapid and complete than the conventional nondegradable plastics that they replace. Further, since all or a major portion of the composition will be poly(lactic acid), and/or a lactic acid derived lactide or oligomer, no residue or only a small portion of more slowly degrading residue will remain. This residue will have a higher surface area than the bulk product and an expected faster degradation rate. Since both lactic acid and lactide can achieve the same repeating unit, the general term poly(lactic acid) as used herein refers to polymers having the repeating unit of formula I without any limitation as to how the polymer was made (e.g. from lactides, lactic acid, or oligomers), and without reference to the degree of polymerization or level of plasticization.

The preferred composition of the present invention comprises polymerized lactic acid units with formula I: wherein n is an integer with a value between about 450 and about 10,000 and the alpha carbon is a random mixture of D and L (or R and S) with a preponderance of one of the pure enantiomers when plasticized by lactic acid, lactide monomers, oligomers of lactide, oligomers of lactic acid, derivatives of oligomeric lactide and various mixtures thereof. A plasticizer may be produced by stopping the reaction before polymerization is completed. Optionally additional plasticizer consisting of lactide monomers (D-lactide, L-lactide, D,L-lactide, or mixtures thereof), lactic acid, oligomers lactide or oligomers of lactic acid or its derivatives including all L-, D-, and DL- configurations, and mixtures thereof can be added to the formed polymer. The more intimately the plasticizer is integrated within the polymer the better are its characteristics. In fact very intimate dispersion and integration is needed to obtain the advantages of the invention as further discussed below. If desired, additional monomer or oligomer plasticizer can be added to any residual monomer or oligomer remaining in the composition after polymerization. The oligomers of lactic acid and oligomers of lactide defined by formula II: where m is an integer: $2 \leq m \leq 75$ (including all L-, D-, DL- configurations and mixtures thereof, both random and block configurations, useful for a plasticizer). The derivatives of oligomeric lactic acid (including all L-, D-, DL- configurations and mixtures thereof, both random and block configurations, useful for a plasticizer) are defined by the formula III: where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated,

where R′ = H, alkyl, aryl, alkylaryl or acetyl, and R′ is saturated,

where R and R′ cannot both be H,

and where q is an integer: $2 \leq q \leq 75$, however, the preferable range is: $2 \leq m \leq 10$. The plasticizers added to the polymer compositions have the following functions:

(a) They act as plasticizers introducing pliability and flexibility into the polymer compositions not found in polymer-only composition.

(b) Addition of these plasticizers to the poly(lactic acid) reduces the melt viscosity of the polymers and lowers the temperature, pressure, and shear rate required to melt form the compositions.

(c) The plasticizers prevent heat build up and consequent discoloration and molecular weight decrease during extrusion forming of poly(lactic acid).

(d) The plasticizers add impact resistance to the compositions not found in the polymer alone.

In addition, the plasticizers may act as compatibilizers for melt-blends of polylactides and other degradable and nondegradable polymers. That is, molten mixtures of two different polymers can more intimately associate and mix into well dispersed blends in the presence of the plasticizers. The plasticizers may also improve performance in solution blending.

The subscripts n, m, p, and q above refer to the average number of mers (the repeating unit) of the polymer or oligomer. Number average molecular weight M_n as used below is related to the mers by multiplying n, m, p, or q by the molecular weight of the individual mer, for poly(lactic acid) this number is 72. The number of mers present in a polymer is also called the degree of polymerization. The reader is referred to the following texts where this subject is discussed further: Polymer Chemistry an Introduction, 2nd Edition, R. Seymour et al,

Marcel Dekker, Inc., 1988 and Introduction to Polymer Chemistry, R. Seymour, McGraw-Hill, New York, 1971.

When n is low, the poly(lactic acid), is easily processable, but is considerably weaker than when n is larger. When n is quite large, e.g., 7000 or greater, the poly(lactic acid) is quite strong but difficult to injection mold. Preferably n is approximately 500 to 3000 for the best balance of melt-processability and end-use physical properties. The amount and type of monomer is selected to obtain L-/D ratios from lactic acid or their cyclic dimer, lactide, as further discussed below. Both lactic acid and lactide achieve the repeating poly(lactic acid) unit, shown above, but lactide is preferred since it more easily obtains the higher molecular weights necessary for good physical properties. Since lactide has two alpha carbons which are assymetric, there are three types of lactide, viz., D,D- (or D-); L, L- (or L-); and meso D,L-lactide.

D-lactide is a dilactide, or cyclic dimer, of D-lactic acid. Similarly, L-lactide is a cyclic dimer of L-lactic acid. Meso D,L-lactide is a cyclic dimer of D- and L-lactic acid. Racemic D,L-lactide comprises a 50/50 mixture of D-, and L-lactide. When used alone herein, the term "D,L-lactide" is intended to include meso D,L-lactide or racemic D,L lactide. The term intimately dispersed as used herein means the material is homogeneously and intimately mixed with the polymer.

Pure poly(L-lactic acid) and poly(D-lactic acid) have poor processing characteristics, easily craze and become opaque. Pure poly(D,L-lactic acid) processes easily but is not a rigid or orientable as the lactide copolymers with a preponderance of D or L configurations. The comonomer ratio of between 85/15 to 95/5 (ratio of L-enantiomer to D-enantiomer would be about 92.5/7.5 to about 97.5/2.5), and most preferably about 90/10, L-lactide/D,L-lactide is a preferred embodiment of the invention. At higher ratios than 95/5, the copolymer is

difficult to thermoform without crazing and easily becomes opaque at room temperature. Also, at ratios above 95/5 the material becomes bimorphic and difficult to extrude because of different crystalline forms that affect the processing conditions. Further, above ratios of 95/5 the material must be processed too close to its decomposition point to obtain reasonable viscosities without color formation. At lower ratios than 85/15, the lactide copolymers exhibit lower moduli than the predominantly L or D copolymers. Further, at ratios below 85/15 it is difficult to obtain a required crystallinity in a reasonable time period. In between these limits the copolymers are quenched from the melt in typical manufacturing/processing equipment of plastics technology to achieve films and moldings which are clear, colorless, and extremely rigid. Their properties as formed, above, are closely matched to those properties of a crystal polystyrene. However, a wider range of L-/D-enantiomeric ratio may be useful for special applications.

Another advantage of this invention is that the all-lactic acid copolymer can utilize inexpensive feedstocks. Corn syrup via starch and corn can be fermented to either L- or racemic D,L-lactic acid, depending on the microorganism. Racemic D,L-lactic acid is cheaply obtainable via ethylene which can be oxidized to acetaldehyde, which is reacted with hydrogen cyanide to form lactonitrile, which is hydrolyzed to racemic D,L-lactic acid. Lactide is simply obtained by distillation of lactic acid. No change of the stereochemistry of the asymmetric carbon occurs in transforming lactic acid to lactide by ordinary distillation/condensation methods.

While the reaction of L-lactide and D,L-lactide is discussed herein, it is to be understood that the reactions specifying L-lactide may also use D-lactide. Thus the reaction of D-lactide and D,L-lactide according to the method described herein will give an equivalent

product; the only difference being that it rotates light in a different direction.

The copolymers of the present invention are preferably formed by heating the mixture of monomers to form a homogeneous melt and adding a catalyst to cause the lactides to undergo a ring-opening polymerization. The polymerization is preferably carried out in an inert, anhydrous, atmosphere, such as nitrogen or argon, or in a vacuum. Suitable catalysts include divalent metal oxides and organo-metallic compounds such as stannous octoate, zinc acetate, cadmium acetate, aluminum acetate or butanoate, tin chloride, tin benzoate, and antimony oxide. Stannous octoate is the preferred catalyst because of its high solubility in the monomers, ease of preparation in anhydrous form, and low toxicity. The amount of catalyst required can vary from approximately 0.02 to 2 percent by weight, based on monomers and is preferably about 0.2 percent. The molecular weight and melt viscosities of the copolymers are controllable by the amount of catalyst and/or chain-transfer agents such as glycolic acid. The reaction temperature of the polymerization is between approximately 100 to 200 C. The least color formation occurs below 140 C and the rate of polymerization is best above 135 C. Since racemic D,L-lactide melts at 127 C it is best for conversion of monomer to polymer to polymerize at a temperature above 127 C.

Where a substantially clear and transparent composition is required, as with crystal polystyrene offsets, the copolymers of this invention are polymerized in an inert atmosphere above their melting points, which are generally in the 125 to 150 C range. The molten lactide copolymer can be extruded from the polymerizer in strands and rods, quenched, pelletized and stored in bags for use in subsequent molding and extrusion operations.

Similarly, clarity of thermoformed packaging films and shaped articles is achieved by molding and extruding above the copolymer's melting points and fast

cooling the fabricated item. Thereafter, the copolymers remain transparent unless heated for several hours above their glass transition temperature, Tg, and below the melting point, Tm. Slow cooling of thermoformed sheets, slabs, films, and molded items can induce spherulite crystallinity in the copolymers which gains improvement in the heat stability of the fabricated item, but causes some loss of transparency. Nucleating agents such as sodium benzoate, calcium lactate, and the like, can also induce rapid and substantial crystallinity. A modest amount of drawing of the copolymer, between its Tg and Tm, induces orientation of the polymer molecules and can substantially improve physical properties without loss of transparency.

Blending of different types of lactide polymer or copolymer can substantially change the physical properties. As an example, the melt-blending of the high-melting L-lactide polymer with a lower melting lactide copolymer can provide a transparent material which has a sufficient amount and type of crystallinity to remain substantially transparent. Those skilled in the art will recognize that transparency in molded films, great stiffness, elevated heat distortion temperature, thermo-processability, and environmental biodegradability are a rare combination of properties. Thus, the polymers can be blended, as well as nucleated, oriented, and controlled by molecular weight to provide a great deal of latitude in the processability and final properties in the final compounded thermoplastic.

The copolymers of the present invention will hydrolyze back to lactic acid in the presence of moisture. In the presence of ambient air and humidity the hydrolysis becomes evident in about 12 to 18 months time. The copolymers then become sticky, somewhat opaque, and very brittle. When immersed in water the copolymers show obvious hydrolysis effects in 1 to 4 months time, depending on the composition, molecular weights, the ambient temperature, their surface-to-volume ratio, and

the particular, aqueous environment the copolymers are placed in. Microorganisms can further reduce the lactic acid to carbon dioxide and water. As an approximate measure, the copolymers have a shelf life of several months, but disappear within about a year when thoroughly wet.

The following examples are merely illustrative of the present invention. In Examples 1B to 7B, a composition series was prepared and evaluated. It was discovered, in contrast to the prior art, that there are distinct differences in the processing behavior and physical properties of the L-lactide/D,L-lactide copolymers.

Example 1B

In a dry, 500 ml, round-bottom flask was charged 160 g of L-lactide (Purac, Inc., "triple-star" grade) and 40 g of racemic D,L-lactide (Purac, Inc., "triple star" grade). This mixture was heated for approximately 1 hour at 123-129 C under a stopper with a continuous nitrogen purge through a stopper inlet and outlet. The monomers form a clear melt, which is mixed thoroughly by swirling the melt. Catalyst solution was prepared and dried by azeotropic distillation, that is, 10 ml of stannous octoate (Polysciences, Inc.) was dissolved in 60 ml of toluene; 10 ml of toluene, with trace water, was distilled to a Dean-Stark trap that was vented via a drying tube. A 0.20 ml quantity of the stannous octoate solution was pipetted into the melt and mixed thoroughly. The nitrogen sweep continues and the melt becomes increasingly viscous over the next 3 hours. Heating continues at 123-127 C for 20-24 hours. The mixture was allowed to cool to room temperature and the flask cooled further with liquid nitrogen behind a shield. The glass shatters and is removed from the polymer by tapping. The copolymer is clear and colorless and is evaluated in a series of tests shown in Table 1B. Films were compression molded at 170 C

in a heated hydraulic press for later tensile testing. Slabs, 1/8 inch thick were molded for impact testing by notched Izod, ASTM, D256 and heat deflection temperature, ASTM, D648. Glass transition temperature (Tg) and melting point (Tm, center of the endotherm) were evaluated by differential scanning calorimetry (DSC).

Examples 2B-7B

The procedures of Example 1B were repeated except that the ratio of L- and racemic D,L-lactide were changed as shown in Table 1B with the test results. The pure L-lactide polymer, Example 7B, would not always mold well at 170 - 200 C since it frequently crazed badly on cooling in the mold. Frequently, on cooling, it opacified. Figures 15-18 illustrate DSC plots from material of Example 5B as further discussed below.

TABLE 1B. PROPERTIES OF L-LACTIDE/RACEMIC D,L-LACTIDE COPOLYMERS

Composition, Weight Ratio, L-Lactide/ D,L-Lactide (Racemic)	80/20	85/15	87.5/12.5	90/10	90/10	95/5	100/0
Example No.	1B	2B	3B	4B	5B	6B	7B
Color/Transparency	Colorless, transparent	-----	-----	-----	----->	White,	opaque
Film Thickness, Mil	10	5	15	11	5	10	5
Tensile Strength, 1000 psi, ASTM D882	7.9	6.9	8.3	8.6	8.2	9.2	(a)
Elongation, %	3.5	5.8	6.0	7.1	7.2	5.1	(a)
Tangent Modulus, 1000 psi	289	221	694	210	268	748	--
Izod Impact Strength[(b)], ft-lb/in.	--	0.44	0.34	0.31	--	0.41	(a)
M_w, 1000's	--	928	--	--	--	--	--
M_n, 1000's	--	218	--	--	--	--	--
T_g, C[(c)]	53	53	48	44	--	46	--
T_m, C[(c)]	--	--	125	133	--	152	190

(a) Crazes on cooling; too brittle to test
(b) Notched samples, impacted on notched side on 1/8-inch thick specimens
(c) Differential scanning calorimetry in nitrogen with 10 C/min. heating rate

Example 8B

Similar to Examples 4B and 5B, a 90/10 weight ratio copolymer of L-lactide/racemic D,L-lactide was prepared. Into a dry, nitrogen-swept, 2-liter flask was placed 1045.8 g L-lactide and 116.4 g of racemic D,L-lactide. A 1.0 ml quantity of anhydrous stannous octoate (0.2 ml per ml of toluene) solution was added. The flask was swept with nitrogen overnight, then heated in a 141 C oil bath until the monomers are melted and well mixed, and the heating decreased slowly to 125 C and continued for 72 hours. The polymer slowly whitens on cooling. After removing the glass, the cloudy, colorless, glassy copolymer was evaluated. Gel permeation chromatography obtains a weight-average molecular weight (M_w) of 522,000, and a number-average molecular weight (M_n) of 149,000.

A DSC of the lactide polymer reveals a strong Tm at 145 C, see Figure 13. The lactide polymer was melted, quenched, and examined again by DSC to reveal no crystallization or melting points. However, a Tg appears at approximately 50-55 C. The results show the polymer can be crystalline or amorphous, depending on its heat history.

Examples 9B-12B

The composition series was extended, using the procedures of Example 1B except other L- and racemic D,L-lactide ratios were used and heating was 2 hours 125 C, 14 hours 125-147 C, then 2 hours 147-131 C. The results are shown in Table 2B.

TABLE 2B. TENSILE AND MODULUS PROPERTIES OF L-LACTIDE AND D,L-LACTIDE COPOLYMERS

Composition, Weight Ratio, L-Lactide/ D,L-Lactide (Racemic)	70/30	60/40	20/80	0/100
Example No.	9B	10B	11B	12B
Color/Transparency	Colorless/ Clear	--	--	--
Film Thickness, Mil	6-9	4-6	4-5	5-7
Tensile Strength[a], 1000 psi, ASTM D638[a]	6.9	6.7	5.8	5.6
Elongation, %	3.2	3.0	2.7	2.8
Tangent Modulus, 1000 psi	287	293	275	278

[a] Films were pulled at a jaw separation of 0.2"/min. and chart speed of 5"/min.

The results of the above examples reveal that only certain compositions have the required properties for a crystal polystyrene offset. The main requirements for a crystal polystyrene-like material are clarity and colorlessness, tensile strength greater than 7000 psi, tangent modulus (a measure of stiffness) greater than 400,000 psi and well-behaved thermoplasticity. Table 3B lists some side-by-side comparisons of a crystal polystyrene (OPS) and a 87.5 weight percent L-lactide and 12.5 weight percent racemic D,L-lactide random copolymer.

TABLE 3B. PHYSICAL PROPERTY COMPARISONS

Property	Poly(lactic acid), Example 3B	Crystal Polystyrene
Impact strength, notched Izod, ft-lb/in.	0.4	0.4
Ultimate tensile strength, psi	8300	7400
Elongation, %	6.0	4.0
Elastic modulus, psi	694,000	450,000
Deflection temperature, F under load, 264 psi	[a]	200
Specific gravity	1.25	1.05
Rockwell hardness	[b]	M75
Vicat softening point, F	[c]	225
Melt flow rate, D1238(G)	40-46[d]	1.7 g/10 min.[e] 1.6 g/10 min.[f]

[a] Depends on heat history
[b] Shore D = 97
[c] DSC, T_m = 125 C (257 F) at 10 degree/min.
[d] Flow rate decreases at lower temperature
[e] Listed by manufacturer
[f] By our experiment

Example 13B

The copolymer of Example 2B was molded and remolded several times to determine if color would develop in the films and the molecular weights remained high. This determines if the copolymer can be recycled, an important consideration for manufacturing practices. The results of Table 4B show that the copolymer remained completely transparent and colorless after repeated heating and molding despite the fact that the copolymer was repeatedly exposed to air at elevated temperatures.

TABLE 4B. EFFECT OF MOLDING ON LACTIDE COPOLYMER

Example No.	History	Appearance	M_w, 1000's	M_n, 1000's	M_w/M_n
Example 2B[(a)]	Not molded, directly from polymerization	Completely transparent and colorless	928	218	--
Example 13B[(a)]	Ex. 2B after molding[(b)]	Completely transparent and colorless	301	135	2.22
Example 13B[(a)]	Ex. 2B after molding 6 times[(b)]	Completely transparent and colorless	137	56.7	2.42

(a) 85/15, L-lactide/racemic D,L-lactide copolymer
(b) Compression molding at 167 C (333 F) for 7 minutes to 5-mil film

<u>Examples 14B-18B</u>

The copolymers of Examples 2B, 3B and 6B were compression molded into films of approximately 20 to 30-mil thickness and were placed in a heated Instron tester where the films were drawn 5 times their length at 83 C at a rate of 0.5 inch per minute. The films were cooled quickly upon removal from the Instron, and found to be approximately 5-mil in thickness. They were clear and colorless. Tensile properties were evaluated and are listed in Table 5B. When drawn 8 to 10 times their length, the films show evidence of crystal formation by virtue of haze development and some loss of transparency.

The results demonstrate that very thin films can be made with adequate stiffness and transparency for a crystal polystyrene offset. Thus, despite the higher density of the lactide copolymers compared to polystyrene, less material can be used for stiff crystal polystyrene offsets.

TABLE 5B. PROPERTIES OF L-LACTIDE/RACEMIC D,L-LACTIDE COPOLYMERS AFTER ORIENTATION[a]

Composition, Weight Ratio, L-Lactide/ D, L-Lactide (Racemic)	85/15	85/15	85/15	87.5/12.5	95/5
Example Number	14B	15B	16B	17B	18B
Film thickness, mil	5.5	5.0	6.5	5.0	4.0
Tensile strength, 1000 psi	14.0	14.7	15.0	13.0	16.0
Elongation, %	31.5	15.4	30.0	23.8	37.4
Tangent modulus, 1000 psi	--	564	419	432	513

[a] 5X oriented at 83 C using a draw down speed of 0.5 in./min. on Instron

Example 19B

Films of the copolymers of lactide of Table 1B were immersed in water for several months interval. The copolymers remained clear for approximately 2 months; after 3 months a slight haziness developed. Upon setting on the shelf in humid air and with frequent handling, the films remain virtually unchanged for approximately 1 year although Instron data will show a slow decrease in the strength and elongation after several months. In a landfill, the buried films disappear in 6 months to 2 years, depending on the moisture, pH, temperature, composition, surface-to-volume ratio, and biological activity of the landfill. All of the films burn with a clean, blue flame.

Example 20B

The lactide copolymer of Example 5B (quenched, compression-molded film) was examined by DSC and found to have less than 2 percent crystallinity, see Figure 8, in the vicinity of 130 C. A 1/8 inch thick sample of the co-

polymer of Example 5B was annealed in a 185 F oven for 16 hours. The sample turned hazy and the DSC of the sample, see Figure 10 revealed a pronounced increase in the crystallinity. The sample showed a 264 psi heat deflection temperature (HDT) of 90 to 95 C. A similar sample without annealing exhibited a heat deflection temperature of 50 to 55 C, which corresponds to its Tg.

Example 21B

Calcium lactate, 5 weight percent, was blended on a heated mill roll with the lactide copolymer of Example 5B at 170 C for approximately 5 minutes. The blend was stripped off the roll as a sheet and examined. It was stiff, strong, and hazy. Optical microscopy at 82X reveals heterogeneous domains in the size range of from a few microns to 30 microns. DSC reveals a substantial increase in crystallinity in the vicinity of 145 C, see Figure 11, which remain on quenching and reheating. The results, above, comparing Examples 8B, 20B, and 21B, show that nucleating agents are more prompt and efficient in inducing crystallinity in lactide copolymers. Nucleating agents such as salts of carboxylic acids may be used, salts of lactic acid are preferred.

Example 22B

In a 500-ml, 3-neck, round bottom flask, equipped with a mechanical stirrer and a nitrogen inlet and outlet, was placed 180.7 g of L-lactide and 40.2 g of racemic D,L-lactide (both Boehringer and Ingelheim, grade S). The contents of the flask were heated to 110 C under a nitrogen sweep to melt the lactides and 20.1 g of polystyrene (Amoco R3, melt index 3.5 g/10 min.) was added. The polystyrene swelled highly and partially dissolved with stirring overnight while advancing the heat to 185 C. The temperature was decreased to 141 C and 0.2 ml of anhydrous stannous octoate solution (0.2 ml/ml of toluene) was added. The stirrer was turned off and the

lactides allowed to polymerize at 141 C over 3 days time. The highly swollen, polystyrene floats to the top after turning off the stirrer. The lower, polylactide phase was cooled and examined by DSC. The sample has a low Tg, approximately 35 C, and is otherwise lacking in apparent temperature transitions. Compression-molded films are clear, colorless, and very pliable. These results indicate that the polystyrene thoroughly interrupts crystallinity formation.

Example 23B

The lactide copolymer of Example 8B was mill-roll blended with 20 weight percent of the homopolymer of L-lactide produced in Example 7B. A sample of the homopolymer was analyzed by DSC, see Figure 14. The blended sample was examined by DSC and found to have a Tg of 59-63 C and strong Tm's at 150 and 166 C, see Figure 15. Films were clear to slightly hazy, depending on their cooling rate after pressing. Quenched samples easi.y crystallize on heating to approximately 80-90 C. As a result the heat deflection temperature of the blend is now quite high. The blend becomes hazy at 80-90 C but does not deflect with heat as does the unblended 90/10 copolymer. Tensile data as shown in Table 6B were obtained on unoriented, compression-molded films and compared to similarly obtained data for polystyrene.

TABLE 6B. COMPARISON OF BLEND OF POLYLACTIDE OF EXAMPLE 23B WITH CRYSTAL POLYSTYRENE

	Example 23B[a]	Crystal Polystyrene[a,b]
Film thickness, mil	8	14
Tensile strength, ASTM D882, 1000's psi	7.7	6.0
Elongation, %, to yield	6.5	3.2
Tangent modulus, 1000's psi	323	267

[a] Thin films, unoriented, compression-molded specimens
[b] Melt Index 1.7

This example illustrates that melt blending is an excellent way to improve the properties of the copolymer so that advantageous properties similar to polystyrene are realized. The higher the amount of homopolymer based on L-lactide (or D-lactide) blended with the polymer the higher will be the heat deflection temperature, however, haziness will also increase. Thus addition of homopolymer may be combined with other methods of increasing polystyrene like properties while still retaining clarity.

As a further example, orienting films produced from the polymer increases the tensile properties. At eight to ten times the draw the physical properties are still increasing but the material becomes hazy. The degree of orientation will thus need to be controlled and combined with the other property changing methods to achieve optimum polystyrene like characteristics.

<u>Examples 24B-27B</u>

Examples 24B to 27B were polymerizations of lactide with controlled amounts of chain transfer agents, demonstrating that molecular weights can be controlled using transfer agents such as glycolic acid. The results are shown in Table 7B. A nearly straight line

relationship exists between the amount of transfer agent and the reciprocal of the weight average molecular weight. Preferred chain transfer agents are lactic acid or glycolic acid.

TABLE 7B. MOLECULAR WEIGHT CONTROL USING CHAIN TRANSFER AGENTS

Example No.	PPH of[a] CTA	M_n[b]	M_w[b]	M_w/M_n
24B	0.22	13,500	107,300	8.0
25B	0.45	12,800	66,700	5.2
26B	0.90	7,300	29,900	4.1
27B	1.80	4,700	13,900	2.9

(a) Parts of glycolic acid chain transfer agent (CTA) per hundred parts of lactide in polymerization recipe.

(b) Gel permeation chromatography in tetrahydrofuran solvent, 23 C, with 10^6, 10^5, 10^4, and 10^3 anhstrom columns, number average, M_n, and weight average, M_w, molecular weights are calculated compared to monodisperse polystyrene standards.

Example 28B

A 4.0-mil, compression-molded film of the lactide copolymer of Example 2B was evaluated as a barrier film by ASTM methods. The results are shown in Table 8B. The lactide copolymer is a much better barrier to carbon dioxide and oxygen than is polystyrene. By comparison to some other polymer barrier films, the lactide copolymer is an adequate barrier film for many packaging applications.

TABLE 8B. EXAMPLE 28B PERMEABILITY TO GASES[a]

Vinylidiene[b] Units	Lactide Copolymer, Example 2B	Crystal[b] Polystyrene	Poly(ethylene terephthalate)	Chloride-Vinyl Chloride Copolymer
cc/100 in.^{2}/ 24-hr./atmos.				
CO_2	32.1	900	15-25	3.8-44
O_2	19.9	350	6-8	0.8-6.9

[a] ASTM D1434-75, Example 2B was a 4.0-mil, compression-molded film.
[b] Values from Modern Plastics Encyclopedia

Example 29B

Sheets, 1/8-inch thick of the lactide copolymers of Examples 1B-6B were immersed overnight in a mixture of petroleum ether and methylene chloride. At ratios of 70/30 to 60/40, petroleum ether/methylene chloride, the copolymers would foam when placed in boiling water. Irregular, but well expanded, foams would form.

Thus, compatible chemical or physical blowing agents may advantageously be used with other processing steps to produce foamed materials. These materials are useful where foamed styrene is typically used (e.g. eating utensils, packaging, building materials and the like). For example, a foaming agent can be added prior to extrusion or injection molding.

Example 30B

A comparison was made of the melt viscosities of a commercial, crystal polystyrene (Type 201, Huntsman Chemical Corp.) and the lactide polymer of Example 8B. The melt index, ASTM D1238 (G), of the polystyrene was 1.6 g/10 min. at 200 C using the standard 5 Kg weight. The melt index of the lactide polymer was 40-46 g/10 min. under the same conditions, however, at 160 C the value was 8.0 g/10 min. A more detailed comparison of melt viscosities was obtained by observing the melt viscosities

of the two polymers in an Instron Capillary Viscometer. The comparative results are shown in Figure 12. The shear rates normally encountered during extrusion and injection molding are approximately 100 to 1000 reciprocal seconds. Inspection of the data of Figure 12 shows that the melt viscosity of the lactide polymer at 160 C is very similar to that of the polystyrene at 200 C.

The above results illustrate that lactide polymers can be melt-processed, at lower temperatures than polystyrene, by very similar methods.

Examples 31B-34B

Small, test polymerizations of purified (recrystallized and dried) mesolactide (meso D,L-lactide) were carried out as the homopolymer and the copolymer. The molecular weights were evaluated by GPC and compared to analogues of D,L-lactide. The results are presented in Table 9B. The polymers were melt pressed into films and their physical properties evaluated and compared as shown in Table 10B. Within experimental differences of sheet thickness and molecular weight, the copolymers are similar within experimental error. The homopolymer of mesolactide is somewhat weaker.

TABLE 9B. GPC MOLECULAR WEIGHT COMPARISONS OF MESO-AND RACEMIC LACTIDE POLYMERS AND COPOLYMERS

Example Nos.	Composition	Res. Mon., %	GPC x 10^{-3}			M_w/M_n
			M_n	M_w	M_z	
31B[a]	D,L-PLA	--	97.5	341	757	3.49
32B	Meso PLA	2.76	62.5	152	264	2.42
33B	90/10, L-/meso	1.67	29	142	301	1.67
34B[a]	90/10, L-/D,L	--	91.3	201	350	2.20

[a] Racemic D,L-lactide

TABLE 10B. PHYSICAL PROPERTY COMPARISON OF RACEMIC D,L- AND MESO D,L-LACTIDE POLYMERS AND COPOLYMERS[a]

Example No.	Polymer Composition	Elastic Modulus, 100 psi	Tensile at Yield Strength, 100 psi	Elongation to Yield, %	Film Thickness, mil	Strain Rate, in./min.
31B	Homopolymer of racemic D,L-lactide	278	5.6	2.8	5-7	0.25
32B	Homopolymer of meso D,L-lactide	345	3.8	3.5	9	0.25
33B	90/10, L-/meso D,L-lactide copolymer	190	7.9	3.8	12-15	0.25
34B	90/10, L-/racemic D,L-lactide copolymer	323	8.6	4.6	4-6	0.25

(a) Compression-molded films

Examples 35B-47B

These examples illustrate the preferred copolymer ratio of the L/D,L polylactide copolymer series (racemic D,L-lactide was used throughout these examples). Of particular interest were the 80/20, 90/10, 95/5, and 100/0 ratios. Each of these copolymers is a material having different properties. Table 11B contains data on the thermal properties of these unoriented copolymers. The glass transition temperature, Tg, varies with the amount of intimately dispersed residual lactide monomer. A typical relationship is shown in Figure 16 where the residual lactide was measured by TGA and the Tg was estimated by DSC. To a close approximation, the Tg follows this relationship for all of the L-/D,L-lactide copolymer ratios. The 80/20 copolymer typically is an amorphous material with a glass transition temperature of 56 C. This copolymer has limited commercial use since its heat distortion temperature will be on the order of 45-50 C, which is considered too low for many packaging applications which require a rigid polymer used in applications up to 70 C.

The other copolymers have the same or only slightly higher glass transition temperatures, but can be crystallized to improve their thermal stability. The rate of crystallization increases as the D,L content decreases and the molecular weight decreases. From the point of view of thermal properties alone the 100 percent poly(L-lactide) polymer is most desirable. However, when other characteristics such as processability into molded and extruded shapes, the capability to do so at lower temperatures with less viscosity and color formation, discharging a reactor, and transparency are taken into account the preferred ratio is 85/15 to 95/5 as further discussed herein.

TABLE 11B. SUMMARY OF THERMAL PROPERTIES OF LACTIDE COPOLYMERS

Ex. No.	Copolymer Ratio	Glass Transition Temperature C	Melting Temperature C
35B	80/20	56	--
36B	90/10	55	150
37B	95/5	59	164
38B	100/0	63	178

The mechanical properties of sheet extruded from each of these copolymers also differs somewhat, depending on copolymer ratio. Table 12B summarizes data that has been obtained on as-extruded and 3x biaxially oriented sheet. The biaxially oriented sheet can be either amorphous or semi-crystalline through crystal growth during annealing. The annealed sheet has been found to be thermally stable up to the annealing temperature, approximately 110 C.

Since the 80/20 copolymer does not crystallize upon annealing, it will always be subject to thermal distortion when heated above its glass transition temperature. Orientation does increase its room temperature mechanical properties to very high levels, however.

The 90/10 copolymer shows an increase in most properties from both annealing and orientation. The oriented and annealed sheet had mechanical properties approximately the same as that of the 80/20 copolymer.

The available data on the mechanical properties of unoriented 95/5 copolymer indicates it is approximately the same strength as the 90/10 copolymer within a generous experimental error, compare, for example, Examples 4B, 5B, and 6B. The mechanical properties of the 95/5 oriented copolymer are not as reproducible as those of either the

80/20 copolymer or the 90/10 copolymer. However, they can be considered acceptable for most applications. The reason for the drop in mechanical properties has been attributed to numerous micro defects found in the oriented sheet. The cause of those defects has never been identified; however, the material is known to craze e. ily upon crystallizing.

For comparison Boehringer Ingelheim poly(L-lactide), Resomer L214, a polymer with a Mw of 800,000 is shown as Examples 38B and 47B. The tensile strength of this polymer is not very different from that of the copolymers examined, but its tangent modulus is considerably higher; however, the values used in the tables were as published values not from the tests used to evaluate the other examples.

TABLE 12B. SUMMARY OF MECHANICAL PROPERTIES OF LACTIDE COPOLYMERS

Ex. No.	Copolymer Ratio	Morphology	Process	Tensile Strength psi	Tangent Modulus psi	Elongation %
39B	80/20	A	E	7,500	305,000	5.7
40B	80/20	A	0-3x	12,200	427,000	18.2
41B	90/10	A	E	8,000	150,000	5.0
42B	90/10	C	E	8,500	188,000	4.6
43B	90/10	A	0-3x	11,700	494,000	41.2
44B	90/10	C	0-3x	10,200	401,000	20.7
45B	95/5	A	0-3x	9,900	273,000	56.5
46B	95/5	C	0-3x	8,800	245,000	68.0
47B	100/0	C	M	9,400	580,000	--

A = Amorphous
C = Crystalline
E = Extruded
M = Molded
O = Oriented

Rheological analysis of the 90/10, 95/5, and 100/0 copolymers was also made to examine the effect of copolymer ratio on flow properties. Because it has a

higher melting point than the copolymers, the 100/0 polymer has to be processed at higher temperatures than the other two materials. With a Mw of approximately 200,000 pure poly(L-lactide) has to be heated to 200 C in order to have a zero shear melt viscosity below 100,000 poise. By way of contrast, the 95/5 copolymer and 90/10 copolymers having Mw's of 200,000 have zero shear viscosity of 100,000 poise at 175 C and 160 C, respectively.

Examples 48B-56B

Processing aids (plasticizers) are necessary in preventing color during extrusion and compounding. The pure poly(lactic acid) can be substantially heated by the work put into it by a high-shear zone of a twin-screw extruder. An extruder set at 350 F, will work on a high molecular weight poly(lactic acid), with no processing aid, to cause its internal temperature to rise to 390 F, or higher, causing browning of the extrudate. For a high shear extruder this can be prevented using approximately 5 percent lactide incorporated into the polymer. It is presently believed that the processing aid acts as a lubricant to prevent discoloration. Other processing aids such as calcium lactate, sodium stearate, and sodium benzoate also are effective. Some illustrative results are shown in Table 13B. To those skilled in the art it will be obvious that the exact amount of processing aid will depend on the molecular weights of the poly(lactic acid) and the amount of shear mixing imposed.

Examples 53B and 54B were discolored because they slightly heat-degraded during compounding. For the above examples, using lactide as processing aid (plasticizer), about 5 percent lactide was required as a minimum processing aid to obtain a colorless product. It is noted that other processing aids such as sodium benzoate and calcium lactate obtain colorless extrudates when used in lower amounts.

TABLE 13B. USE OF PROCESSING AIDS

Example	Co-polymer[a] Composition	Processing Aid Type	Processing Aid Wt. %	Melt Zone[b] Temp. F	Color of Extrudate
48B	95/5	Lactide	15.5	391	Colorless
49B	90/10	Lactide	15.0	381	Colorless
50B	90/10	Lactide	12.4	385	Colorless
51B	92.5/7.5	Lactide	8.1	374	Colorless
52B	90/10	Lactide	6.5[c]	381	Colorless
53B	90/10	Lactide	4.6	390	Slightly brown
54B	90/10	Lactide	3.4	404	Brown
55B	90/10	Sodium benzoate	2.0	378	Colorless
56B	90/10	Calcium lactate	2.0	384	Colorless

[a] Monomer ratio, L-/racemic D,L-lactide
[b] Temperature at high-shear zone in twin-screw extruder

Example 57B

Examples 57B to 75B teach the incorporation of lactide in conjunction with quenching to obtain pliability and transparency. Alternatively, the polymers can be annealed to improve stability against heat distortion.

Poly(L-lactide) was prepared by methods previously described. Thus 300 g of triply recrystallized and thoroughly dried L-lactide was loaded into a clean, flame-dried, argon-cooled, 500 ml round-bottom flask. The flask was fitted with a rubber septum and inlet and outlet syringe needles that admitted a continuous argon purge. Stannous octoate solution was prepared by dissolving 20 g in 110 ml of toluene, previously dried over molecular sieves, then distilling 10 ml toluene in order to azeotropically dry the solution. The final concentration was 0.2 g/ml stannous octoate in toluene. A 0.3 ml quantity was injected through the septum onto the L-

lactide. The flask and its contents were placed in a 150 C oil bath, and when melted, swirled vigorously to obtain a homogeneous mix. The argon purge continued and a thermocouple was fitted through the septum into the melt. The melt was 143 C. The temperature of the oil bath was advanced to 200 C and heating and light purge continued for 20 hours. The temperature of the melt advances to 170-174 C in the first two hours of heating. The final temperature was 170 C. After 20 hours of heating the flask was cooled in air to room temperature and the solid polymer was transparent.

Polymer was recovered by shocking the flask with dry ice to free it from the glass. The residual monomer was analyzed by thermogravimetric analysis and the molecular weights by gel permeation chromatography. Differential scanning calorimetry reveals a glass transition temperature (T_g) at 53 degrees and two melting point endotherms with peaks at approximately 170 and 190 C. The gel permeation chromatography molecular weights: M_n = 129,000; M_w = 268,000; M_z = 462,000; M_w/M_n = 2.08. Residual monomer by thermogravimetric analysis was 2.3 percent, (Example 57B, Table 14B.) The experiment shows that L-lactide can be polymerized above, or near, its melting point and the products remain transparent and more amorphous.

Example 58B

By methods similar to Example 57B, 104.0 g of L-lactide was polymerized using 0.10 ml of stannous octoate catalyst solution. However, the reaction temperatures were 155-165 C for 72 hours. The polymer (Example 58B of Table 14B) slowly crystallizes upon forming and is a white opaque solid at reaction or room temperature. Since the sample was smaller than that formed in the preceding experiment, the polymer cooled more quickly, but it did not quench to a transparent solid. In comparison to Example 57B, the lower reaction temperature permits the

poly(L-lactide) to crystallize and become opaque, thus an intimate dispersion of plasticizer does not form.

The temperature is slowly advanced in many of these experiments to accommodate the polymerization exotherm. The reaction temperature must reach at least 170-175 degrees prior to a substantial monomer-to-polymer conversion, otherwise the poly(L-lactide) crystallizes and is difficult to remelt.

In Examples 60B-66B the polymerization of L-lactide was repeated varying the conditions to obtain poly(L-lactides) with different residual lactide contents and crystallinities. The results are shown in Table 11B, where it is seen that pliability and toughness were obtained only when the product has been quenched from the melt, is transparent at room temperature, and contained approximately 10 percent or more residual lactide. It is believed that the L-lactide homopolymer must be polymerized in the melt, and quenched from the monomer-polymer melt temperatures, to a transparent material as evidence of its homogeneous and intimately plasticized properties. When the poly(L-lactide) crystallizes during polymerization because the polymerization temperature is well below the polymer's melting point, the residual monomer is no longer effective as a plasticizer. If the polymer crystallizes upon cooling to room temperature, it also loses its plasticization. Annealing at elevated temperatures will restore crystallinity to amorphous samples.

TABLE 14B. POLYMERIZATION OF L-LACTIDE

Ex. No.	Catalyst Amount pph	Temp C	Time Hours	Polymer Appearance	Residual Monomer Percent	Sample Size g
57B	0.02	156-201[a] 150-174[b]	20	clear transparent, hard, glassy	2.30	300
58B	0.02	155-165[a]	72	crystalline, opaque, hard, brittle	--	104
59B	0.005	120-200[a] 111-200[b]	24	crystalline, opaque, hard, brittle	--	100
60B	0.02	135-145[a] 135-152[b]	22	crystalline[d], opaque, hard, brittle	1.1	500
61B	0.02	117-185[a] 120-175[b,c]	24	crystalline, opaque, hard, brittle	1.74	100
62B	0.02	160-170[a]	8	crystalline, opaque, hard, brittle	2.18	2,000
63B	0.02	145[a] 137-144[b]	15	crystalline, opaque, hard, brittle	3.6	25
64B	0.0553	190[a] 160-215[b]	0.3	clear, pliable, tough, transparent	10.1	25
65B	0.0553	188-193[a] 147-200[b]	0.28	clear, transparent, pliable except at edge of polymerizate	22.9	25
66B	0.02	145[a] 150-133[b]	2.75	crystalline[d], opaque, hard, brittle	52.5	25

[a] Oil bath temperature
[b] Polymer melt temperature
[c] This polymer crystallized at 160-169 as the temperature was advanced, and it did not remelt.
[d] Transparent at reaction temperature; crystallizes upon cooling.

This transparency and intimacy of association between polymer and monomer is also affected by the ratio of L/D,L-lactide. At approximately 95/5 ratio the copolymer easily quenches to a transparent solid. The 90/10 ratio, L/D,L-lactide copolymer quenches quite easily. The 100 percent L-lactide polymer quenches with difficulty from thick sections of the polymer to a transparent material. Some comparisons are shown by Examples 67B-71B of Table 15B. Thinner cross sections, i.e., films of the L-lactide polymer can be plasticized and quenched to pliable and transparent materials. The 80/20 copolymer quenches very easily to a transparent solid. The latter has only a trace of crystallinity as seen by differential scanning calorimetry.

TABLE 15B. TRANSPARENCY OF LACTIDE POLYMERS

Ex. No.	Lactide L/D,L-Ratio	Temp., C[a]	Time, Hours	O/T[b]	GPC M_w	Residual Monomer, percent
67B	95/5	145-160	67	SO	385,000	2.64
68B	100	135-152	22	O	322,000	1.1
69B	90/10	150-157	45	T	821,000	4.95
70B	90/10	150-170	48	T	278,000	1.37
71B	80/20	135-175[c]	23	T	--	--

(a) Melt temperature (polymerization temperature)
(b) Opaqueness/transparency (O/T) after air-cooling of polymerizates; opaque (O); slightly opaque (SO); transparent (T)
(c) Slow-cooled for 1 hour

All D,L-lactide is racemic.

All of the lactide polymers thermoform easily, that is, when heated by a radiant heater until soft, then sucked down on an intricate mold, they all form the pattern of the mold easily. However, the poly(L-lactide) becomes partially cloudy and hazy upon cooling. The 95/5,

90/10, and 80/20 copolymers are quite clear and transparent throughout their thermoforms.

Example 72B

The poly(L-lactide) from Example 57B was melted and mixed on an open 2-roll mill for 5 minutes at 375 F (190 C), then compression molded at 375 C for 2 minutes, then air-quenched to room temperature in approximately 30 seconds. Both 7-and 20-mil thick films were prepared. Both were clear and transparent without trace of haze or opacity. Residual monomer in the film was 0.79 percent. The films are very stiff.

Example 73B

The experiment was repeated except that the milling was continued for 10 minutes instead of 5 minutes. The films were analyzed by thermogravimetric analysis again and found to have 0.38 percent lactide. The films were clear, transparent, and stiff.

Example 74B

The mill-rolled polymer was also compression molded into a 1/4 x 1/2 x 1 inch plaque. This plaque required 5-10 minutes to cool in the press by turning on the cooling water to the press. The plaque was white, opaque, and crystalline except for the extreme edges, which were transparent.

The above Examples 72B-74B teach the quenching of films of poly(L-lactide) to maintain transparency. When cooled more slowly, they crystallize and lose their transparency.

Quenching as used herein indicates that the temperature is dropped rapidly to prevent extensive crystallization of the polymer. Crystallization of polymers is a slow process, requiring minutes to hours to fully accomplish. When this is desired, the temperature is held above the glass-transition temperature, Tg, for

some time to allow the molecules to order themselves into extensive crystalline lattices. This is called annealing. When cooled rapidly from an amorphous melt, the polymer does not have the time required and remains largely amorphous. The time required to quench depends on the thickness of the sample, its molecular weight, melt viscosity, composition, and its Tg, where it is frozen-in as a glassy state. Note that melt viscosity and Tg are lowered by plasticization and favor quenching. Thin films obviously cool very quickly because of their high surface-to-volume ratio while molded items cool more slowly with their greater thicknesses and time spent in a warm mold before removal. Regular structures such as poly(L-lactide) order more easily and crystallize more quickly than more random structures such as a copolymer.

With the polylactides the melting points are approximately 150-190 C depending on the L-lactide content and, therefore, the regularity of structure. The Tg of all the polylactides, including various L and D,L homopolymers and copolymers is 60 C. The Tg decreases when residual lactide is intimately dispersed with the polymer. Quenching to an amorphous state requires that the polymer or copolymer in an amorphous melt is rapidly cooled from its molten state to a temperature below its Tg. Failure to do so allows spherulitic crystallinity to develop, that is, crystalline domains of submicron to micron size. The latter scatters light and the polymer specimens become opaque. These crystalline forms have improved stability to heat distortion. This spherulitic crystallinity is often called short range order-long range disorder since the crystallites are separated by amorphous regions. However, the crystallites act as pseudo crosslinks to maintain dimensional stability above the Tg but below their melting points. Alternatively stability to heat distortion can be obtained by orienting an amorphous polymer above its Tg but below its melting point. Here, the polymer molecules are stretched to allow

some long range ordering, then "heat set" to permit the ordering to complete, that is, given some time to anneal. The amorphous polymer is thereby crystallized into a different order, called long-range order, short range disorder. Transparency and resistance to heat distortion are favored.

A detailed discussion can be found in textbooks, for example, "Structural Polymer Properties", by Robert J. Samuels, Wiley Publications, NY, NY 1974.

As D,L-lactide is introduced as a comonomer, quenching can be replaced by ordinary cooling to retain transparency. Spherulitic crystallinity can be introduced into these films by annealing and the 100 percent L-lactide polymer is the fastest to crystallize. Where transparency is not required the higher L-lactide polymers can be annealed to greatly improve their resistance to thermal distortion. Conversely, where transparency is required, such as in a crystal polystyrene offset, great care must be taken to avoid this type of opaque crystallinity.

Example 75B

The poly(L-lactide) film samples were annealed on a hot plate at 240 F (115 C). The film turned hazy in approximately 1 minute and completely cloudy in approximately 2 minutes. By way of comparison, a 90/10, L/D,L-lactide copolymer film required 10 minutes to turn hazy, 15 minutes to become completely cloudy. When suspended by one end horizontally in an oven and advancing the temperature slowly, the annealed poly(L-lactide) sample remained straight until a temperature of 295 F (146 C) was obtained. The film then bent over. The annealed 90/10 copolymer bent over at a temperature of 185 F (85 C). The results show that the amount of crystallinity of polylactides can increase their form-stability at elevated temperatures to a temperature that is well above their T_g.

Examples 76B-79B

The following examples illustrate the beneficial effects of adding lactide during compounding. The examples show that without lactide as modifier, the lactide polymer degrades during compounding. With the addition of lactide both discoloration and molecular weight decrease are prevented or substantially reduced during compounding.

Thus, in Example 76B, a 90/10, L-/D,L-lactide copolymer prepared as described by previous methods using 0.02 pph $SnCl_2 \cdot 2H_2O$ catalyst was ground and extruded into pellets from a twin screw compounder, adding 5 weight percent lactide. The melt zone temperature of the extruder rose to 390 F, the polymer discolored, and the weight average molecular weight (M_w, by gel permeation chromatography) decreased by approximately 40 percent. The results indicated that insufficient lactide was added for this very high M_w copolymer. The results are shown in Table 16B. The pellets from this compounding were recompounded adding a further 10 weight percent lactide (Example 78B). The melt zone temperature was 375 F, and the results were much better: further discoloration did not occur, molecular weight decreased slightly, or within experimental error, and a pliable composition was obtained.

TABLE 16B. EFFECT OF LACTIDE AS MODIFIER DURING COMPOUNDING

Ex. No.	Before Compounding Color	M_w[(a)]	M_w/M_n[(a)]	Lactide[(b)] weight percent
76B	Light yellow	513	2.15	0.78
77B	Light yellow	278	1.80	1.37

Ex. No.	After Compounding Color	M_w[(a)]	M_w/M_n[(a)]	Lactide[(b)] weight percent
76B	Dark yellow	322	2.05	5.56[(c)]
77B	Yellow	184	1.90	2.26
78B	Dark yellow	307	2.00	14.4[(d)]
79B	Colorless[(e)]	324	1.99	14.6

(a) GPC x 10^{-3}
(b) By thermogravimetric analysis, at 200 C
(c) Five weight percent lactide added during compounding.
(d) Further 10 weight percent lactide added during compound.
(e) Thin film

To ascertain that the second compounding and extrusion were facilitated due to the lactide modifier and not the decreased molecular weight, another compounding (Example 77B) was performed starting with a similar-M_w copolymer of 90/10, L-/D,L-lactide. In this case, no lactide was added back in during the compounding. The melt zone temperature was 382 F, the copolymer was discolored, and the M_w decreased by approximately 66 percent. In addition, approximately 5 percent more torque was required to compound the mix of M_w 278,000 as compared to the one of M_w of 322,000 with added lactide.

After compounding twice with lactide, Example 78B was analyzed by thermogravimetric analysis and found to have a lactide content of 14.4 percent. The material of Example 78B was converted to a blown film by means of a Haake-Brabender extruder in Example 79B. Thin films of this composition are colorless, highly transparent, and

very pliable and extensible as described below in Examples 60B-64B. The Mw by gel permeation chromatography was 324,000 (cf. Mw = 307,000 before compounding and extrusion). The Tg of this plasticized material is 42 C and differential scanning calorimetry reveals a very small amount of crystallinity melting at approximately 138 C. The amount of lactide present is 14.6 percent as estimated by thermogravimetric analysis.

Examples 80B and 81B

The compounded polylactides, Example 76B and 77B, were mixed together in the twin-screw compounder with extra lactide to raise the lactide level to approximately 20 percent. The compounding temperature was 347 F (175 C), much reduced from the previous 375 to 385 F. The compounding proceeded smoothly without further discoloration.

The above results clearly show the beneficial effects of added lactide as modifier. The required torque to compound the compositions, the discoloration, and the working temperature are decreased when adding lactide. Further evidence of plasticization is seen in the lowered Tg and the pliability of the compositions. In addition, molecular weight decreases are avoided and stable compositions are obtained. It will be obvious to those skilled in the art that the amount of lactide employed depends on many factors, including the desired amount of plasticization sought, the type of compounder that is used, and the molecular weight of the polylactides.

Examples 82B-86B

These examples illustrate plasticization with oligomeric esters of poly(lactic acid). Copolymers of 90/10, L-/racemic D,L-lactide were melt blended with added lactide, esters of oligomeric/lactic acid, and mixtures thereof. They were characterized by tensile and thermal properties.

In Example 82B, a control copolymer of 90/10, L-/racemic D,L-lactide was assayed by thermogravimetric analysis to be 6.74 percent lactide. This was mixed with 30 percent by weight oligomeric poly(methyl lactate) (Mella) in Example 83B, which was prepared by heating 2,500 g of (S)-methyl lactate in an autoclave at 210 C for 3 hours, then collecting the Mella which fractionally distilled at 81 to 85 C/1.25 torr. The mixture was melt blended on an open 2-roll mill at approximately 350 F. The blend was compression molded in a press at approximately 350 F into clear, pliable films. The tensile properties, before and after, adding the Mella are recorded in Table 17B. The glass transition temperature (Tg) was reduced by the Mella plasticizer.

For Example 84B, the 90/10, L-/racemic D,L-lactide copolymer was melt blended with added L-lactide in a twin screw extruder to adjust the L-lactide content to 20 percent by weight. The blend was further mixed with oligomeric poly(ethyl lactate) (Ella) (Example 85B) and Mella (Example 86B). The properties of these blends are also recorded in Table 17B.

TABLE 17B. CHARACTERISTICS OF POLYLACTIDES[a] PLASTICIZED WITH OLIGOMERIC ESTERS OF LACTIC ACID

Ex. No.	Plasticizer	Elastic Modulus psi	Break Strength psi	Strain at Break, %	T_g[b]	T_m[c]
82B	6.74%[d] L-lactide	370,000	6,903	2	51	141
83B	6.74%[d] L-lactide and 30% Mella[e]	154,000	2,012	100	30	141
84B	20% L-lactide	101,000	2,637	278	--	--
85B	20% L-lactide and 30% Ella[f]	7,316	2,561	339	--	--
86B	20% L-lactide and 30% Mella[e]	3,620	495	83	--	--

(a) 90/10, L-/racemic D,L-lactide copolymer
(b) Glass transition temperature
(c) Melting point
(d) Analyzed by thermogravimetric analysis
(e) Methyllactate oligomer
(f) Ethyllactate oligomer

Examples 87B-92B

These examples illustrate the injection molding of polylactide copolymers and the process for increasing their heat distortion temperature.

90/10 L-/racemic D,L-lactide copolymer (about 1.3 weight percent residual monomer) was injection molded on a New Britain injection molding machine having 75 tons of clamping capacity and a maximum shot size of 6 ounces. Standard ASTM D-638 tensile bars were molded during these trials. The molding conditions were varied over a range of conditions. The polymer, having a weight average molecular weight of 350,000 was successfully molded to melt temperatures between about 165 and 200 C. Polymers with lower molecular weights were more easily molded. The temperature of the mold ranged between about 23 and about 85 C, and the time at which the polymer was held in the mold after filling, but prior to ejection, was varied between about 10 seconds and about 2 minutes.

Calcium lactate, at a 1 weight percent concentration, was compounded into the polymer before injection molding. This was done to provide nucleation sites to increase the rate of crystallization. Crystallization in the injection molded parts was desirable to increase the heat distortion temperature of the polymer.

For example, molded parts of the nucleated 90/10 copolymer, were annealed between metal plates at about 110 C for times between about 30 seconds and about 4 minutes. After examining the DSC curves of the annealed parts for the presence and degree of crystallinity, it was found that annealing times between about 1 and 2 minutes were required to develop full crystallization when the polymer is in contact with solid walls at 110 C. Mechanical properties of injection molded samples are shown in Table 18B. This table shows that annealing does affect the heat distortion temperature, but does not strongly influence the strength, modulus, or elongation to break. The heat distortion temperatures listed in this table were obtained under a load of 264 psi. If a 66 psi condition had been used to determine heat distortion temperatures, the increase observed for the annealed sample would have been even greater.

TABLE 18B. MECHANICAL PROPERTIES OF INJECTION MOLDED POLYLACTIDE

Example Number	Process	Strength, psi	Modulus, psi	Elongation, percent	HDT, C
87B	Injection	8600	230,000	6	46
88B	Injection /annealed	8700	258,000	4	57

Calcium lactate-nucleated polymer was injection-molded with a mold maintained at about 85 C and holding times of about 2 minutes. These conditions were

insufficient to develop full crystallinity in the sample. The mold heating system was improved to provide in mold annealing at temperatures higher than 85 C, most preferably between about 110 and about 135 C.

Samples were also injection molded using a melt blend of the 90/10 L-/racemic D,L-lactide copolymer and about 5 to about 20 weight percent poly(L-lactide) as nucleating agent. The results are shown in Table 19B. The injection molded specimens were well formed with excellent strengths, stiffness, and impact resistance. The heat distortion temperatures shown in Table 19B can be improved by annealing.

TABLE 19B. PROPERTIES OF INJECTION MOLDED BIODEGRADABLE POLYMER

Ex. No.	Formulation[a] 90/10 %	L-PLA %	Tensile Strength, psi	1% Secant Modulus, psi	Strain to Break, %	HDT 264 psi F	Izod Impact ft-lb/in.
89B	95	5	8,245	227,440	7	115	0.34
90B	90	10	8,325	221,750	7	117	0.34
91B	85	15	8,631	230,150	7	116	0.35
92B	80	20	8,615	228,840	6	117	0.35

[a] 90/10 = 90/10, L-/racemic D,L-lactide copolymer; L-PLA = 100 percent L-lactide polymer

Examples 93B-109B

Note: Examples 93B to 109B listed in Tables 20AB and 20BB contain information identical to Examples 65 to 81 in Tables 15A and 15B of section A. General First Embodiment. The information is repeated here for convenience in discussing these examples in relation to section B. Second General Embodiment.

Comparative Examples 93B to 109B were selected from the patent literature that presented conditions most likely to result in materials of the invention. The materials produced in these patents were not completely

characterized, thus experiments were needed to allow a more complete characterization of the examples and provide meaningful comparisons that would demonstrate that the materials of the present invention are indeed novel.

With regard to the present invention, compositions were sought that had residual lactide or lactic acid contents of about 0.1 to about 60 weight percent and in addition may have the lactide or lactic acid intimately dispersed within the polymer. The results fall into obvious categories. Thus, products with number-average molecular weights, M_n, less than 32,000 do not have the physical properties required in the present invention. In fact films from these low M_n compositions were too brittle to be handled for tensile measurements.

It is known from the teachings herein that lactic acid, lactide or oligomers of lactide or lactic acid, or derivatives of lactic acid must be present to provide plasticization and the advantages of the invention. The plasticizer must be present in amounts greater than about 0.10 weight percent up to about 10 weight percent. Thus, if the plasticizer is intimately dispersed and effectively mixed, the composition is substantially transparent. The heterogeneous domain size of the lactic acid, lactide, oligomer, or oligomeric derivative is small enough, generally less than one micron, so that it will no longer scatter light, i.e., it is intimately dispersed. Conversely, white opaque samples are always hard because they have crystallized under the test conditions. Crystallization squeezes the lactide out of the polymer mass, resulting in hard stiff compositions that are a gross mixture of monomer and polymer. This is also obvious from differential scanning calorimetry (DCS) measurements. Monomeric lactide that has segregated reveals itself with a separate melting point at 95 to 100 C, whereas well-plasticized samples do not show a distinct monomer melting point.

One very important point is that the cited patents frequently specify L-lactide homopolymer ("100 percent L-" in Tables 20AB and 20BB). The homopolymer of L-lactide easily crystallizes because of its high melting point. At lower reaction temperatures, the homopolymer can retain appreciable quantities of monomer, but the composition freezes during polymerization. At higher, melt temperatures, the L-lactide polymerizes so quickly that it is very difficult to stop the polymerization with substantial monomer left in the product. This is true to a lessor extent for poly(L-/ D,L-lactide) copolymers also.

Inspecting the results listed in Table 20AB and 20BB reveals that the comparative examples obtain either products with low residual lactide, or products with residual lactide that is not intimately dispersed as seen by their color, opaqueness, and crystallinities. Thus, Example 94B (very similar also to the work of Schneider), obtained no residual lactide while Example 97B had 4.6 weight percent residual lactide, and both were off colored products. The best known laboratory techniques were added to the procedures, described in the footnotes, for these examples, from a historical standpoint (monomer purity, for example) in an effort to make the procedures work, with indifferent success. Either glassy, or hard, crystalline, opaque products were obtained. It should be noted that only those examples using tin compounds as catalysts appear to be acceptable for many packaging applications.

It appeared particularly that the methods of US 2,758,987 and US 4,137,921 would provide the materials of the present invention. To ascertain this, it was necessary to do the listed experiments on their teachings in detail as shown in Examples 94B and 97B. Preparations according to the exact replication of the methods were performed. Thermogravimetric analysis reveals 0.0 percent residual lactide for one such preparation, Example 94B. Whereas this polymer was light yellow and contains no

detectable residual lactide, the composition of the present invention is colorless and contains small amounts of lactide as a processing aid to prevent color formation during melt fabrication.

A colored product was obtained repeating the teachings of Example 97B. The residual monomer analyzed as 4.6 percent lactide. The material was light yellow, presumably due to the high polymerization temperature which produced color bodies with the lactide polymer, the dioxane solvent, and stannous octoate.

TABLE 20AB. RELATED ART POLYMERIZATIONS OF LACTIDE CONDITIONS

Ex. No.	Patent	Pat. Ex.	Lactide Monomer (s)	Catalyst		Polymerization	
				Type	pph	Temp. C	Hours
93B	2,758,987	1	L-	PbO	0.30	150	42
94B	2,758,987	3	50/50 L-/D,L	PbO	3.00	150	89
95B	3,982,543	3	L-	PbO	0.30	150	31
96B	DD 14548	2	L-	SnO[a]	0.009	193	3
97B	4,137,921	4	90/10 L-/D,L	$Sn(Oct)_2$, GA/ dioxane[b]	0.0553	180 190 210	0.33 0.33 0.33
98B	GB 755,447	4	D,L	ZnO[c]	0.02	150	24
99B	GB 755,447	2	D,L	Zn Powder[d]	0.02	140	25.5
100B	GB 755,447	6	D,L	Zn Carbonate Hydroxide[c]	0.02	140 150	2 3
101B	CA 932,382	1	D,L	Tetraphenyl Tin	0.02	165	20
102B	CA 923,245	1,7 & 8	L-	Et_2Zn	0.167	105-110	2
103B	DE 946,664	2	D,L[e]	$ZnCl_2$	0.25	140	48
104B	DE 1,112,293	1	L-	Sn Stearate	0.0087 as Sn	205-210	0.5
105B	2,951,828	1	L-[f]	$SnCl_4$ suspension[g]	0.30	160	5
106B	3,268,487	2	D,L	Tris(2-chloroethyl)amine[h]	0.88	80	24
107B	EP App. 108,635 (1984); 4,550,449; 4,539,981	6, Polymer 8	L-	$Sn(Oct)_2$	0.00108	165	93
108B	4,539,981; 4,550,449	Polymer 33	L-	$Sn(Oct)_2$	0.00119	136-139	64
109B	4,539,981; 4,550,449	Polymer 37	L-	$Sn(Oct)_2$	0.00324	115	64.5

(a) No reaction until recipe was changed by adding 0.75 pph of 88 percent lactic acid. Product was white, opaque, very hard and brittle; film too brittle to handle.
(b) Included was glycolic acid as chain transfer agent.
(c) Insoluble
(d) Insoluble after 24 hours plus additional 1.5 hours with 700 μl 88 percent lactic acid and 100 μl H_2O.
(e) In toluene; product colorless and very viscous.
(f) In mineral spirits, Stoddard solvent No. R-66.
(g) Agglomerated
(h) In dioxane containing 0.517 pph KOH; no polymerization.

TABLE 20BB. RELATED ART POLYMERIZATIONS OF LACTIDE RESULTS

Ex. No.	Residual Monomer, Percent	GPC x 10^{-3}			M_w/M_n	Polymerizate Appearance
		M_n	M_w	M_z		
93B	0	254	454	717	1.79	Light yellow, crystalline, opaque
94B	0	97	187	322	1.94	Light yellow, transparent
95B	0.85	95	195	325	2.06	Partially opaque crystalline, partial transparent
96B	17.5(a) 7.1; 7.7	5 7	7 8	9 10	1.47 1.25	White, crystalline, opaque
97B	4.6	116	218	356	1.88	Light yellow, transparent
98B	47.7	--	--	--	--	White, crystalline (monomer), opaque
99B	65.3	--	--	--	--	White, crystalline (monomer), opaque
100B	79.6	--	--	--	--	White, crystalline (monomer), opaque
101B	1.4	116	214	340	1.84	Yellow, transparent
102B	1.9	80	150	235	1.87	Orange, crystalline, opaque
103B	5.4[i] 2.5; 1.9[j]	164 307	377 527	657 808	2.3 1.72	Hard, colorless
104B	43.3	30	35	41	1.17	Hard, crystalline, opaque
105B	8.6; 9.6	219	343	504	1.57	Hard, crystalline, opaque
106B	100	--	--	--	--	All crystalline monomer
107B	5.0	14	26	35	1.88	White, crystalline, opaque
	film[k]	14	26	35	1.82	Some transparency at edges
108B	20.2[l]	Greater than 1,000,000				White, crystalline, opaque
109B	32.2[m]	Greater than 1,000,000				White, crystalline, opaque

[i] Sample heated at 140 C, then 5 minutes in 60 C vacuum oven to remove solvent.
[j] Sample heated overnight in 60 C vacuum oven to remove solvent.
[k] Transparent, very stiff and brittle.
[l] Tunc obtains 17.1 percent, very high molecular weight.
[m] Tunc obtains 28.0 percent, very high molecular weight.

Compositions having n equal to an integer between 450 and 10,000 have a good balance between strength and melt processability and are preferred. If a monomer is selected as a plasticizer a unique composition may be obtained by adding monomer that is stereochemically different from that used to obtain the polylactide in the composition. Similarly, addition of oligomer stereochemically different from that which may be obtained during polymerization of the polymer gives a unique product. As taught herein the products are colorless in the absence of coloring agents. Color bodies can be excluded by performing the polymerization in an inert atmosphere and at reaction temperatures preferably at 140 C or below and by appropriate choice of plasticizer in the composition as described above. During melt processing, a sufficient amount of plasticizer is intimately mixed to prevent discoloration and degradation of molecular weight. Various combinations of the above treatments can be employed to obtain the optimum characteristics as those skilled in the art will appreciate, once knowing the teachings of the invention.

As can be noted in section A. First General Embodiment above, a higher amount of plasticizer can have significant effect. In the present application, lower amounts of plasticizer are preferred to impart stiffness. Plasticizer present in an amount of between about 0.1 and about 10 weight percent is preferred. The plasticizer can remove molding strains, lubricate, maintain a lower processing temperature, maintain a lower melt viscosity, preserve transparency during melt forming, and regulate degradation time. The composition contains plasticizer in an amount that depends on polymerization conditions or on the amount added after polymerization. The additional material used as plasticizer may be selected from the group: lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof. Oligomers of lactide or lactic acid, or oligomeric

derivatives of lactic acid, may also be added. Unique compositions may be obtained by addition of monomer different from those selected for the polymers in the composition or oligomers different from those obtained during the polymerization.

Contemplated equivalents of the compositions of the invention are those that contain minor amounts of other materials. The compositions produced in accordance with the present invention can be modified, if desired, by the addition of a cross-linking agent, nucleating agent, other plasticizers, a coloring agent, a filler and the like. Further treatments such as biaxial orientation and heat treatment provide for a useful film that is a replacement for polystyrene.

After treatment there is obtained a biaxially oriented and annealed environmentally decomposable polylactide film or sheet suitable for use as a substitute for biaxially oriented crystal polystyrene film or sheet comprising, a film or sheet of a copolymer of the formula I, where n is between about 450 and about 10,000 prepared from about 85 and 95 weight percent D-lactide or L-lactide and between about 5 and about 15 weight percent D,L-lactide, said film having intimately dispersed therein the residue of a modifier selected from the group consisting of lactic acid, D-lactide, L-lactide, D,L-lactide, oligomers of said acid and said lactides, and mixtures thereof, said oriented and annealed film having a tensile strength in excess of 7,500 a tangent modulus in excess of 350,000, a Tg below about 60 C and the capacity of being dimensionally heat stable at temperatures of at least 70 C.

The compositions herein can be processed by melt fabrication into useful articles of manufacture having a self supporting structure such as disposable containers, eating utensils, trays, plates, drinking cups, single serving trays, syringes, medical trays, packaging films and the like. The compositions are useful in that they

can have the characteristics of the usual plastics (eg. polystyrene) and therefore substitute for them yet degrade in the environment. The amount of plasticizer serves not only as a processing aid, but also governs the initial physical properties. In addition, the amount of plasticizer governs the environmental degradation rate. The compositions are especially useful for articles having only a one time use or a short life span in use before disposal.

Those skilled in the art will now recognize that there are contemplated equivalents for minor amounts of the polymerized lactide and monomeric lactide. These include glycolide, caprolactone, valerolactone, and other cyclic esters as monomers, and the same and/or open chain aliphatic esters as plasticizers.

C. Third General Embodiment

The present invention discloses the blending of poly(lactic acid) (PLA) with polystyrene (PS), polyethylene (PE), polyethylene terephthalate (PET), and polypropylene (PP). The invention discloses that poly(lactic acid) is melt compatible with these conventional thermoplastics and the effect on their physical properties. Since both lactic acid and lactide can achieve the same repeating unit, the general term poly(lactic acid) as used herein refers to polymers having the repeating unit of the formula I without any limitation as to how the polymer was made (e.g. from lactides, lactic acid, or oligomers), and without reference to the degree of polymerization or level of plasticization.

The environmentally degradable compositions disclosed herein are at least partially degradable. That is the poly(lactic acid) portion of the composition will decompose relatively rapidly compared to the more stable portions of the blend and cause a physical deterioration of the blended material. For example, when the compositions are intimate and homogeneous blends with

small domain sizes the physical deterioration will destroy the original formed product. The compositions herein provide environmentally acceptable materials because their physical deterioration and degradation is much more rapid than conventional nondegradable plastics. Further, since a significant portion of the composition can be poly(lactic acid), and/or a lactic acid derived lactide or oligomer only a small portion of more slowly degrading thermoplastic residue will remain (e.g. polystyrene). This residue will have a high surface area and is expected to decompose faster than a bulk formed product.

D-lactide is a dilactone, or cyclic dimer, of D-lactic acid. Similarly, L-lactide is a cyclic dimer of L-lactic acid. Meso D,L-lactide is a cyclic dimer of D- and L-lactic acid. Racemic D,L-lactide comprises a 50/50 mixture of D-, and L-lactide. When used alone herein, the term "D,L-lactide" is intended to include meso D,L-lactide or racemic D,L-lactide. Poly(lactic acid) may be prepared from one or more of the above.

Example 1C

Polystyrene was solvent blended with poly(lactic acid) and solvent cast from CH_2Cl_2 to determine optimum compatibility. The solvent cast films were translucent and apparently "noncheesy". A sample, appears homogeneous to the naked eye and resists folding and handling without shredding apart. Optical microscopy at 310X reveals heterogeneous domains of 3 microns and less. The blend is apparently very compatible. It exhibits no change over 2 years with regard to "blooming" of fugitive material nor does its physical properties show evidence of degradation.

Example 2C

Polypropylene 8525, Hercules, was similarly melt blended in the Brabender with poly(lactic acid) at 400 F. Ratios of PP/PLA prepared were 100/0 for the control, 90/10, and 75/25.

Examples 3C-5C

Melt blends were prepared of poly(lactic acid) with polystyrene. Both a high molecular weight polystyrene (Piccolastic, E-125, Hercules) and a low molecular weight polystyrene (Piccolastic, D-100) were investigated. Also used was a general purpose polystyrene, (Huntsman polystyrene 208), a crystal polystyrene. These were mixed in a Brabender at 325 F at different ratios with poly(lactic acid).

The polystyrene/poly(lactic acid) ratios used were 100/0 for the control, and 90/10, and 75/25 for the Huntsman 208, general purpose polystyrene.

Examples 6C-7C

Two types of polyethylene terephthalate were used. (Goodyear's "Clearstuff" and Eastman's Kodapak TN-0148). These were dried overnight at 90 C and melt blended at 525 F in a Brabender with poly(lactic acid) for only a few minutes. The poly(lactic acid) reduced the melt viscosity.

Examples 8C-16C

The controls and blends for polypropylene, general purpose polystyrene, and polyethylene terephthalate (Eastman's) from Examples 2C-7C were ground in an Abbey grinder and compression molded into approximately 5 mil films. Polypropylene-poly(lactic acid) films were molded at about 400 F; polystyrene-poly(lactic acid) films were obtained at 250-300 F; polyethylene terephthalate-poly(lactic acid) films were molded at about 525 F. After conditioning at 50 percent r.h. and 23 C for 24 hours they were tested on the Instron. The controls were similarly treated. Samples of the compression molded film were placed in an Atlas Weather-O-Meter for weatherability evaluation (cycles of 102 minutes of sunshine and 18 minutes of rain). The results for these examples are shown in Table IC.

Examples 17C-19C

Three samples of 100 percent poly(lactic acid) using poly (D,L-lactic acid) were prepared as above but with film thicknesses of 10-15 mil. Tests were performed as in Examples 20C-27C below except that the second sample was tested after 82 hours of exposure to 50 percent relative humidity at 72 F.

Examples 20C-27C

High density polyethylene, HDPE, (0.960 g/cc) was melt blended with poly(lactic acid) in the Brabender Plasticorder at 151 C for 10 minutes. Blend ratios of high-density polyethylene/poly(lactic acid) of 100/0 for the controls, 90/10, 80/20, and 50/50 were used. Two samples of each were prepared. The blends were ground in an Abbey grinder and compression molded into 10-15 mil films. The films were tested in an Atlas Weather-O-Meter set for 51 minutes of carbon arc light and 9 minutes of water spray. Temperature was varied from ambient to 140 F. Tensile strengths, elongation to yield tests and classification of the tensile failure were performed for the samples as shown in Table 2C.

Examples 28C-33C

Low density polyethylene, LDPE, (0.917 g/cc) was melt blended with poly(lactic acid) in the Brabender Plasticorder at 151 C for 10 minutes. Blend ratios of low density polyethylene/poly(lactic acid) of 100/0 for the controls 90/10 and 50/50 were used. Two samples of each were prepared. The samples were treated and evaluated as in the case of Examples 20C-27C. Results are shown in Table 2C.

Example 34C

In a 500-ml, 3-neck, round bottom flask, equipped with a mechanical stirrer and a nitrogen inlet and outlet, was placed 180.7 g of L-lactide ɛ d 40.2 g of racemic D,L-

lactide (both Boehringer and Ingelheim, grade S). The contents of the flask were heated to 110 C under a nitrogen sweep to melt the lactides and 20.1 g of polystyrene (Amoco R3, melt index 3.5 g/10 min.) was added. The polystyrene swelled highly and partially dissolved while stirring overnight and advancing the heat to 185 C. The temperature was decreased to 141 C and 0.2 ml of anhydrous stannous octoate solution (0.2 ml/ml of toluene) was added. The stirrer was turned off and the lactides allowed to polymerize at 141 C over 3 days time. The highly swollen, polystyrene floated to the top after turning off the stirrer. The lower, polylactide phase was cooled and examined by differential scanning calorimetry (DSC). The sample has a low Tg, approximately 35 C, and is otherwise lacking in apparent temperature transitions. Compression-molded films are clear, colorless, and very pliable. These results indicate that the polystyrene thoroughly interrupts crystallinity formation under these conditions.

<u>Example 35C</u>

Poly(lactic acid) was mill roll blended with crystal polystyrene. The blend revealed excellent compatibility of polystyrene dispersed in poly(lactic acid). Thus 5 weight percent of polystyrene was dispersed in a 90/10 ratio of L-/racemic D,L-lactide copolymer in a two roll mill at 170 C. The material became hazy and exhibited considerable crystallinity by thermal analysis. This example demonstrates that under these conditions polystyrene easily induces crystallinity in poly(lactic acid). A thermal analysis of the material, see Figure 17, reveals that the material remains crystalline even when heated and cooled.

The Examples 34C and 35C illustrate that poly(lactic acid) blended with the environmentally nondegradable plastics herein can produce final properties

in the mixture depending on the mixing or blending technique used.

Brabender melt-blends of all types exhibited small heterogeneous particle sizes of 10 microns or less. The tensile strengths were evaluated before, and after, simulated weathering. After 1248 hours (52 days) in the Atlas Weather-O-Meter all of the polypropylene samples were whitened, extremely brittle and were not able to be tested. The polypropylene samples were retested at shorter intervals as shown in Table 1C. At approximately 300 hours of weathering in the Atlas Weather-O-Meter, the samples exhibited significant environmental degradation.

The polystyrene blends with poly(lactic acid) exhibited environmental degradation that was apparent after 300 hours of simulated weathering. The polyethylene terephthalate blends were also visibly environmentally degraded in approximately 300 hours.

TABLE 1C. TENSILE STRENGTH OF FILMS BEFORE, AND AFTER ACCELERATED WEATHERING[a]

Blend Ratio and Material	Tensile Strength[b]/% Elongation		
	Before	After, Hours	
		310	400
100/0 PP[c]/PLA	1665/61.0	585/1.6	494/1.7
90/10, PP/PLA	1568/51.0	954/3.2	346/--
75/25, PP/PLA	1124/14.0	370/1.1	254/1.0
100/0 PS[d]/PLA	3200/2.0	1066/1.0	--
90/10, PS/PLA	2350/2.0	582/1.0	--
75/25, PS/PLA	1493/1.6	484/1.0	--
100/0 PET[e]/PLA	3036/--	3509/3.0	--
90/10, PET/PLA	2147/--	1378/3.0	--
75/25, PET/PLA	2743/--	2041/3.0	--

(a) Weather-o-meter, cycle of 102 minutes of sunshine, 18 minutes of rain
(b) 0.05 in./min., on the Instron
(c) Hercules polypropylene 825
(d) Huntsman 208
(e) Tennessee Eastman, Kodapak TN 0148

The poly(lactic acid), high density polyethylene, low density polyethylene, and their blends were evaluated for physical strength, before, and after simulated weathering and the results are shown in Table 2C.

TABLE 2C. PHYSICAL PROPERTIES OF POLYETHYLENE (PE), POLYLACTIC ACID (PLA), AND THEIR BLENDS, BEFORE, AND AFTER, WEATHER-O-METER EXPOSURES

Material[a]	Material Blend Ratio[b] Polymer/PLA	Weather-O-Meter[c] Exposure, Hours	Tensile Strength, psi	Elongation[d] to Yield, %	Type of Tensile Failure
100% PLA[e]	0/100	0	6,030	2.2	Brittle
100% PLA	0/100	0[f]	5,670	2.1	Brittle
100% PLA	0/100	82	(Too brittle to test)	--	Brittle
100% HDPE[g]	100/0	0	3,540	8	Ductile
100% HDPE	100/0	233	1,400	1	Brittle
HDPE/PLA	90/10	0	3,480	7	Ductile
HDPE/PLA	90/10	233	1,720	1	Brittle
HDPE/PLA	80/20	0	3,180	4	Brittle
HDPE/PLA	80/20	125	2,150	2	Brittle
HDPE/PLA	50/50	0	2,720	2	Brittle
HDPE/PLA	50/50	233	(Too brittle to test)	--	Brittle

(a) Compression-molded films, 10-15 mil thickness
(b) Melt-blended in Brabender Plasticorder for 10 minutes, 151 C
(c) 51 minutes of carbon arc light and 9 minutes of water spray for each 1-hour cycle. Temperature varies from ambient to 140 F.
(d) Elongation at maximum in strain curve
(e) Poly(D,L-lactic acid), $\{\eta\}$ = 1.16 dl/g, 25 C, THF
(f) After 82 hours exposure to 50% R.H., 72 F
(g) High-density polyethylene; density 0.960 g/cc; melt index 0.6 g/10 minutes

TABLE 2C. PHYSICAL PROPERTIES OF POLYETHYLENE (PE), POLYLACTIC ACID (PLA), AND THEIR BLENDS, BEFORE, AND AFTER, WEATHER-O-METER EXPOSURES (Continued)

Material[a]	Material Blend Ratio[b] Polymer/PLA	Weather-O-Meter[c] Exposure, Hours	Tensile Strength, psi	Elongation[d] to Yield, %	Type of Tensile Failure
100% LDPE[h]	100/0	0	1,320	80	Ductile
100% LDPE	100/0	125	1,250	67	Ductile
LDPE/PLA	90/10	0	1,190	31	Ductile
LDPE/PLA	90/10	125	855	14	Ductile
LDPE/PLA	50/50	0	1,160	4	Ductile
LDPE/PLA	50/50	125	(Too brittle to test)	--	Brittle

(a) Compression-molded films, 10-15 mil thickness
(b) Melt-blended in Brabender Plasticorder for 10 minutes, 151 C
(c) 51 minutes of carbon arc light and 9 minutes of water spray for each 1-hour cycle. Temperature varies from ambient to 140 F.
(d) Elongation at maximum in strain curve
(h) Low-density polyethylene; density 0.917 g/cc; melt index 0.25 g/10 minutes

The poly(lactic acid) and its blends were much more environmentally degradable than the pure low density or high density polyethylene. The high density polyethylene samples degraded substantially without weight loss while the high density polyethylene-poly(lactic acid) blends exhibited weight loss, particularly where microscopy revealed poly(lactic acid) was exposed at the surface of the films. The high density polyethylene degraded by exposure to actinic light as shown by microscopy.

With all of the samples, increasing the percentage of poly(lactic acid) decreased the tensile strength before, and after, simulated weathering. The incorporation of poly(lactic acid) introduced a faster degradation in blends of polypropylene, polystyrene, polyethylene terephthalate, and high and low density polyethylene. Presumably, the actinic light as well as hydrolysis of the polyesters degrades the polymer. The small size of the spherical, microheterogeneous, domains of the blend are undoubtedly poly(lactic acid), which is mostly buried. Therefore, poly(lactic acid) hydrolysis is slow. Faster degradation via hydrolysis can be achieved by controlling the location of the poly(lactic acid). This, in turn, is related to the rheology of the blend during melt blending. The small size of the dispersed, heterogeneous domains indicates good compatibility of the mixed polymers.

In a simulated landfill, where light is excluded, the controls and the blends show much slower rates of degradation. With hydrolysis, alone, the poly(lactic acid) samples slowly whiten, while the blends are qualitatively unchanged for the time period tested.

Conversely, addition of minor amounts of nondegradable thermoplastics to poly(lactic acid) to form compatible blends, using, for example, polypropylene, polystyrene, polyethylene terephthalate and high and low density polyethylene will retard the degradation rate of

the poly(lactic acid). A preferred compositional range is from 80-99 weight percent poly(lactic acid).

A general description of the environmentally degradable composition comprises blends of a physical mixture of poly(lactic acid) (polylactide), and a polymer selected from the group consisting of a poly(ethylene terephthalate), a polymer or copolymer of styrene, ethylene, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof. Other possible compositional blends are listed below in the discussion of process embodiments of the invention. While the level of plasticizer can vary over wide ranges depending on the amount of poly(lactic acid) present and the type of coblended polymer, the preferred amount for a stiff material is generally about 0.1 to about 10 weight per cent.

The blends preferably use a physical mixture of poly(lactic acid) of the formula I: where n is an integer between 75 and 10,000; and a polymer selected from the group consisting of polystyrene, polyethylene, poly(ethylene terephthalate), and polypropylene and other compositions further discussed below. The composition of poly(lactic acid) in the composition may vary over wide limits such as about 1/99 to about 99/1. A preferred composition is that where the poly(lactic acid) comprises 5 to 50 weight percent of the composition. Another preferred composition has a poly(lactic acid) content of about 10 to 20 weight percent, and another about 80 to 99. The ratio will depend on desired characteristics.

The polymers and copolymers selected from the group above, deemed the added polymer, can be used alone or in combination. The group is not restricted to those cited above since other polymer types are noted as compatible with poly(lactic acid). These include the polymers and copolymers comprised from the group of ethylene, propylene, styrene, vinyl chloride, vinyl acetate, alkyl methacrylates, and alkyl acrylates. It

should be understood that the term copolymers as used herein includes polymers made from mixtures of the monomers in the listed group. Physical mixtures of the polymers and copolymers of the above group are likewise useful in the invention.

A first embodiment of the process for producing the composition includes providing a poly(lactic acid); selecting a polymer from the group consisting of a poly(ethylene terephthalate), a polymer or copolymer of styrene, ethylene, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof; and blending the polymers. The blending may be by melt blending on a mill roll or by compounding in an extruder or by other mechanical means. The poly(lactic acid) provided preferably has the formula I and contains plasticizers as discussed herein.

A second embodiment of the process for producing the composition of the invention includes providing a lactide selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof; selecting a polymer from the group consisting of the polymers or copolymers of styrene, ethylene, ethylene terephthalate, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof. The selected lactide and polymer are mixed and heated to melt the lactide and at least partially dissolve the polymer. Finally, the lactide, is at least partially polymerized to obtain a blend of polylactide, unpolymerized lactide monomer and the selected polymer. The polymerization is preferably controlled by monitoring the amount of lactide remaining and stopping the polymerization at the desired level. If desired, the polymerization can be carried to completion. Additional lactide monomer or other plasticizers such as lactic acid, oligomers of lactic acid, oligomers of lactide, and mixtures thereof, where the oligomers are defined by the formula II: where m is

an integer: $2 \leq m \leq 75$, where the oligomers preferably have a number average molecular weight below about 5,400 and most preferably below about 720; as well as one or more derivatives of an oligomer of lactic acid defined by the formula III: where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated,
where R′ = H, alkyl, aryl, alkylaryl or acetyl, and R′ is saturated,
where R and R′ cannot both be H,
and where q is an integer: $2 \leq q \leq 75$, can be added to obtain desired characteristics as taught in parts A and B above. Additionally, the various types of plasticizers discussed herein and in the other general embodiments provide for: (a) more effective compatibilization of the melt blend components; (b) improved processing characteristics during the blending and processing steps; and (c) control and regulate the sensitivity and degradation of the polymer by moisture.

It will be obvious to those skilled in the art that the proportions of poly(lactic acid) and the added polymer can vary widely depending on their mutual solubilities. Solubilities, in turn, vary with the thoroughness of mixing and the mixing temperature. While placing both the poly(lactic acid) and the added polymer into a mutual solvent solution will obtain intimacy, the use of solvent is impractical for many commercial processes. Physical mixing, such as melt blending on a mill-roll or extruder is more practical, but must be controlled to achieve an intimate dispersion, that is, high shear is required to achieve the desired intimacy. Even with intimate mixing different polymers may not be compatible, that is, they may still separate into relatively large heterogeneous domains of, for example, 10 to 100 micron size, or larger. This results in a "cheesy" mixture, or a blend with poor properties. What is surprising is that poly(lactic acid) is easily blend

compatible with a wide variety of other polymers, including both polar and nonpolar polymers.

The temperature of the melt blending of the poly(lactic acid) with other polymers may be varied to adjust the proportions of the poly(lactic acid) with one, or more, added polymers. At lower temperatures, the solubilities may not be adequate, while too high a temperature will cause decomposition of the mixture. A general temperature range is 100-220 C, and the preferred range is 130-180 C. Equally significant is the melt viscosities of the different polymer components. With increasing molecular weight, the viscosities increase sharply. By controlling the proportions of the poly(lactic acid) and the added polymer, or polymers, the temperature, the mixing type and time, and the molecular weight, a wide range of mixtures can be obtained. Thus, for example, the poly(lactic acid) can be dispersed into the added polymer, or polymers, or vice versa, and the size and geometry of the dispersed phase varied greatly, ranging from discrete spheres to strands of different diameters or lengths. This results in a wide latitude of physical properties and degradation times in the environment. The weight percent ratio of poly(lactic acid) to the selected polymer can be between 99:1 to 1:99.

Where the lactide monomer is used to dissolve the added polymer and the lactide is subsequently polymerized, the temperature of mixing and polymerizing must be balanced between the mutual solubilities and the reactivity of the lactide. Higher temperatures generally produce lower molecular weight poly(lactic acid). A further embodiment of the invention is to mix at one temperature and polymerize at another temperature to achieve variations in the geometry of the dispersed phase, as discussed above.

The compositions herein can be processed by melt fabrication into useful articles of manufacture having a self supporting structure such as disposable containers,

eating utensils, trays, plates, drinking cups, single serving trays, syringes, medical trays, packaging films and the like. The compositions are useful in that they can have the characteristics of the usual plastics and therefore substitute for them yet degrade in the environment. The compositions are especially useful for articles having only a one time use or a short life span in use before disposal.

D. Fourth General Embodiment

Within the scope of the invention is included those impact modifiers which are elastomeric discrete, intimately bound and the polylactic (or polylactide)/impact modifier blend is hydrophobic, nonporous, nonswellable in water, and hydrolyzes at the same rate or slower than the poly(lactic acid) (or polylactide) alone; and melt compatible with poly(lactic acid). By "melt compatible", it is meant all those polymers which can be intimately mixed with poly(lactic acid) as discussed in section C. Third General Embodiment. The mix would result in a substantially homogeneous blend. All of the examples herein exhibit these properties. Since both lactic acid and lactide can achieve the same repeating unit, the general term poly(lactic acid) as used herein refers to polymers having the repeating unit of the formula I without any limitation as to how the polymer was made (e.g. from lactides, lactic acid, or oligomers), and without reference to the degree of polymerization or level of plasticization.

The environmentally degradable compositions disclosed herein are at least partially degradable. That is the poly(lactic acid) portion of the composition will decompose relatively rapidly compared to the more stable portions of the blend and cause a physical deterioration of the blended material. For example, when the compositions are intimate and homogeneous blends with small domain sizes the physical deterioration will destroy

the original formed product. The compositions herein provide environmentally acceptable materials because their physical deterioration and degradation is much more rapid than conventional nondegradable plastics. Further, since a major portion of the composition will be poly(lactic acid), and/or a lactic acid derived lactide or oligomer only a small portion of more slowly degrading elastomer residue will remain (e.g. segmented polyester). This residue will have a high surface area and is expected to decompose faster than a bulk formed product.

The examples below show the blending of poly(lactic acid) (PLA) with a Hytrel™, a segmented polyester which is a block copolymer of hard crystalline segments of poly(butylene terephthalate) and soft long-chain segments of poly(ether glycol). It is shown that poly(lactic acid) is melt compatible with this elastomer and the effect on its physical properties.

D-lactide is a dilactide, or cyclic dimer, of D-lactic acid. Similarly, L-lactide is a cyclic dimer of L-lactic acid. Meso D,L-lactide is a cyclic dimer of D- and L-lactic acid. Racemic D,L-lactide comprises a 50/50 mixture of D-, and L-lactide. When used alone herein, the term "D,L-lactide" is intended to include meso D,L-lactide or racemic D,L-lactide. Poly(lactic acid) may be prepared from one or more of the above.

Example 1D

A polylactide copolymer without Hytrel™ segmented polyester was prepared using the procedure from Example 1B of section B. Second General Embodiment and tested for Izod impact strength. Results are shown in Table D. For further comparison, Table 1B of the Second General Embodiment lists the Izod impact strength of other ratios of L-lactide to D-L lactide.

Example 2D

Into a 3-neck, 250 ml, round-bottom flask is weighed 10.96 g of D,L-lactide, 108.86 g of L-lactide, and 5.27 g of Hytrel™ 4056 segmented polyester (Du Pont, a thermoplastic elastomer). Hytrel™ 4056 segmented polyester is a polyester elastomer with a Shore D durometer, low flexural modulus, high melt viscosity, a melt index of 7, a sp. gr. of 1.17, a m.p. 334 F, a vicat softening temperature of 234 F, and an extrusion temperature of 340-400 F. The flask is fitted with a mechanical stirrer and a nitrogen inlet and outlet. The contents are heated by means of an oil bath. The Hytrel™ segmented polyester dissolves in the molten lactides at 170 C. A catalyst solution is prepared by dissolving 10 ml of stannous octoate in 60 ml of toluene and distilling 10 ml into the toluene. A 100 microliter portion of the catalyst solution is injected into the solution of lactide and Hytrel™ segmented polyester. The mixture is stirred under nitrogen at 155 C for approximately 64 hours.

The viscosity increases sharply and the mixture turns cloudy. The product is tough and opaque. Films of 8-9 mil thickness were compression molded at 155 C and the tensile properties measured, as shown in Table D.

Slabs, 1/8 inch thick, were compression molded and their Izod impact strength measured using a 2 pound pendulum. The results are recorded in Table D where the data are compared to a similar polylactide copolymer of Example 1D without Hytrel™ segmented polyester, and to data for so-called medium-impact polystyrene, Example 7D.

Example 3D

800.0 g of L-lactide and 202.3 g of racemic D,L-lactide are copolymerized using 1.0 ml of the catalyst solution by methods similar to Example 2D, omitting the Hytrel™ segmented polyester. The lactide copolymer is clear and colorless. In a separate polymerization 104.0 g of L-lactide is melt polymerized using 100 microliters of

catalyst. The polymer ,poly(L-lactic acid), is white, crystalline, and crazes easily when struck.

An electrically-heated, 2-roll mill is heated to 375 F, then 8.4 g of Hytrel™ segmented polyester and 19.2 g of poly(L-lactic acid) are banded on the roll. To this was added 172.4 of the lactide copolymer. The mixture blends easily and is removed from the rolls, molded, and tested as in Example 2D. The data are recorded in Table D.

Example 4D

The lactide copolymer of Example 3D, 80 g, the poly(L-lactic acid) of Example 3D, 10 g, and 10 g of Hytrel™ 4056 segmented polyester are 2-roll, mill-blended as described previously in Example 3D. The blend was tested as before and the data are recorded in Table D.

Example 5D

100 g of the blend of Example 3D was further blended with 20 g of Hytrel™ 4056 segmented polyester. The mixture easily mixed on the roll and was apparently quite compatible. The physical properties were measured as described previously and recorded in Table D.

Examples 6D and 7D

Typical crystal polystyrene and medium-impact polystyrene were tested and used for comparative controls.

The above results clearly indicate that polylactides can be impact-modified. The blends provided significantly higher Izod impact strengths than the crystal polystyrene control and gave slightly lower or equivalent impact strengths compared to medium-impact polystyrene. Those skilled in the art will recognize that the data on impact-strength in Table D can be improved further by optimizing the amount and type of impact modifier.

Since polylactides have been shown to be blend-compatible with numerous other compounds and thermoplastics in section <u>C. Third General Embodiment</u>, the process of impact-modifying polylactides is generic to mixtures of polylactides and elastomers that are blend-compatible. Also, those skilled in the art will recognize that the data of Table D will improve as the blends are injection-molded, as opposed to compression-molded, since the former often induces orientation of the specimens and, consequently, a profound improvement in impact strength.

TABLE D. PHYSICAL PROPERTY COMPARISONS OF IMPACT-MODIFIED POLYLACTIDES

Example No.	Composition, weight percent			Tensile Strength, psi[b,c]	Elongation, percent	Tangent Modulus, psi	Izod Impact Strength, ft-lb/in.[c]
	Lactide Copolymer	L-lactide Homopolymer	Hytrel™[a]				
1D	80[d]	20	0	7,667	3.4	322,679	0.3-0.4
2D	95.8[e]	0	4.2[f]	8,636	3.1	359,409	0.40
3D	86.2[g]	9.6	4.2[h]	7,823	3.1	346,502	0.51
4D	80.0[g]	10.0	10.0[h]	--	--	--	0.53
5D	71.2[g]	7.9	20.9[h]	--	--	--	0.61
6D[i]	0	0	0	6,118	3.2	267,245	0.18
7D[j]	0	0	0	6,090	4	--	0.7

(a) DuPont Hytrel™ 4056: a thermoplastic polyester elastomer
(b) ASTM D 882, 7-15 mil film thickness
(c) Compression-molded specimens
(d) Control, 90/10, L-D/L-lactide copolymer
(e) 91/9, L-D/L-lactide copolymer
(f) Hytrel™ dissolved in lactide monomers before 170 C polymerization
(g) 80/20, L-D/L-lactide copolymer
(h) 2-Roll mill-blend at 185-190 C
(i) Control, crystal polystyrene, melt-index 1.7
(j) Control, medium-impact polystyrene

The compositions are useful thermoplastics that can be melt fabricated by conventional processes such as extrusion and molding.

The blends preferably use a physical mixture of poly(lactic acid) of the formula I: where n is an integer between 75 and 10,000; and a polymer comprising a segmented polyester. The poly(lactic acid) content may vary over a wide latitude such as between about 1 and about 99 weight percent. A useful composition is that where the poly(lactic acid) comprises 50 to 99 weight percent of the composition. A preferred composition has a poly(lactic acid) content of 70 to 80 weight percent, while other useful compositions include about 5 to about 20 weight percent, depending on the final use of the composition.

Two embodiments of the general process for producing the composition include (1) melt blending of poly(lactic acid) with a blend compatible polymer that provides improved impact resistance and is discrete and intimately bound (such as a segmented polyester); and (2) solution blending during poly(lactic acid) polymerization as in Example 2D where Hytrel™ segmented polyester is dissolved in the poly(lactic acid). The poly(lactic acid) provided preferably has the formula I. If desired, plasticizer in pliable forming amounts may be added to the blend that is selected from the group consisting of lactide monomer, lactic acid oligomer, lactic acid, and mixtures thereof. The oligomers are defined by the formula II: where m is an integer: $2 \leq m \leq 75$, and is preferably $2 \leq m \leq 10$. Other plasticizer that may be added include one or more derivatives of an oligomer of lactic acid defined by the formula III: where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated,

where R′ = H, alkyl, aryl, alkylaryl or acetyl, and R′ is saturated,

where R and R′ cannot both be H,

and where q is an integer: $2 \leq q \leq 75$, and is preferably. Preferably q is an integer: $2 \leq q \leq 10$. Addition of plasticizer will provide additional unique physical properties and processing advantages as discussed in sections A, B, and C above.

The plasticizers may be present in any amount that provides the desired characteristics. For example, the various types of plasticizers discussed herein and in sections A, B, and C above provide for (a) more effective compatibilization of the melt blend components so that greater intimacy is achieved; (b) improved processing characteristics during the blen ing and processing steps; and (c) control and regulate the sensitivity and degradation of the polymer by moisture. For pliability, plasticizer is present in higher amounts while other characteristics such as stiffness are enhanced by lower amounts. The compositions allow many of the desirable characteristics of pure nondegradable polymers. In addition, the presence of plasticizer facilitates melt processing, prevents discoloration, and enhances the degradation rate of the compositions in contact with the environment. The intimately plasticized composition should be processed into a final product in a manner adapted to retain the plasticizer as an intimate dispersion in the polylactic acid and/or its coblended polymer for certain properties. These steps can include: (1) quenching the composition at a rate adapted to retain the plasticizer as an intimate dispersion; (2) melt processing and quenching the composition at a rate adapted to retain the plasticizer as an intimate dispersion; and (3) processing the composition into a final product in a manner adapted to maintain the plasticizer as an intimate dispersion. The plasticizers are preferably at least intimately dispersed within the polylactic acid if not in the coblended polymer.

Microscopic examination of the Hytrel™ segmented polyester/poly(lactic acid) mixture revealed that the

dispersed Hytrel™ segmented polyester is present in small spherical domains a few microns or less in size. These domain sizes can be adjusted by the mixing conditions such as time, speed of mixing, and temperature.

Therefore, for example, the polymer, or polymers, added to the poly(lactic acid), should be generally of small, heterogeneous domain size, less than 10 microns, and can be submicroscopic, or dissolved, in the poly(lactic acid). In addition, this impact modifier must be elastomeric.

While not wishing to be held to any particular theory, it is believed that the present invention provides a continuous matrix of poly(lactic acid) containing intimately mixed microscopic domains of Hytrel™ segmented polyester that act as crack arresters since the latter is a thermoplastic elastomer compatible with poly(lactic acid).

For this purpose, the impact modifier must be elastomeric and intimately bound into the poly(lactic acid) as a discrete heterogeneous phase. The added polymer, the impact modifier, can be a thermoplastic elastomer, or a crosslinked rubber, to achieve this elastic behavior. Examples are natural rubber and styrene-butadiene copolymers.

Further examples of impact modifiers useful in the invention include polyisoprene (gutta percha), styrene-isoprene-styrene block copolymers, acrylonitrile-butadiene-styrene block copolymers, styrene-ethylene-styrene block copolymers, propylene-ethylene-propylene block copolymers, propylene-isoprene-propylene block copolymers, mixtures thereof, and the like. Polyurethanes that are not significantly water swellable or water soluble may also be used.

In a test of material placed in water for five months, the material embrittled compared to a material not exposed to water. In addition the water turned acidic indicating breakdown of poly(lactic acid) to lactic acid.

It was further apparent that poly(lactic acid) alone degraded faster than the Hytrel™ segmented polyester/poly(lactic acid) mixture. Thus Hytrel™ segmented polyester can also be used to retard the degradation rate of poly(lactic acid).

A third component can be added which is compatible with the other components discussed above to achieve improved compatibility. Thus, where the poly(lactic acid) and the impact modifier have poor compatibility, a third component can be added to improve the compatibility. This third component is usually added where it is compatible with the other two, individually, and where the other two, poly(lactic acid) and impact modifier are not very compatible. This works by increasing the interfacial bonding between poly(lactic acid) and elastomeric impact modifier. However, what is surprising is the wide latitude of compatibility of poly(lactic acid) with other polymer types, both polar and nonpolar. This can be referred to in section <u>C. Third General Embodiment</u> above.

If desired, minor amounts of plasticizer such as glycolide, poly(glycolic acid), caprolactone, and valerolactone may be added.

The compositions herein can be processed by melt fabrication into useful articles of manufacture such as containers, eating utensils, trays, plates, drinking cups, single serving trays, syringes, medical trays, and the like. The compositions are especially useful for articles having only a one time use or a short life span in use before disposal.

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While the invention has been described above with reference to various specific examples and embodiments, it will be understood that the invention is not limited to such illustrated examples and embodiments and may be variously practiced within the scope of the claims hereinafter made.

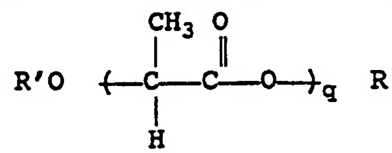
CLAIMS

We claim:

1. An environmentally biodegradable composition useful as a replacement for thermoplastic polymer compositions comprising:

a. a poly(lactic acid); and

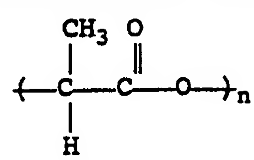
b. a plasticizer of one or more oligomeric derivatives of lactic acid, selected from the group defined by the formula:



where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated,
where R′ = H, alkyl, aryl, alkylaryl or acetyl, and R′ is saturated,
where R and R′ cannot both be H,
where q is an integer: $2 \leq q \leq 75$; and
wherein the plasticizer is intimately dispersed within the polymer.

2. The composition of Claim 1, wherein q is an integer: $2 \leq q \leq 10$.

3. The composition of Claim 1, wherein the poly(lactic acid) is a polymer of the formula:



wherein n is the number of repeating units and n is an integer, $150 \leq n \leq 20,000$.

4. The composition of Claim 1, wherein the composition is unoriented and has a tensile strength of about 300 to about 20,000 psi, an elongation to failure of about 50 to about 1,000 percent, and a tangent modulus of about 20,000 to about 250,000 psi.

5. The composition of Claim 1, wherein the composition is unoriented and has a tensile strength of

about 1,200 to about 4,000 psi, an elongation to failure of about 100 to about 800 percent, and a tangent modulus of about 20,000 to about 75,000 psi.

6. The composition of Claim 1, wherein the composition is unoriented and has a tensile strength of about 4,500 to about 10,000 psi, an elongation to failure of about 100 to about 600 percent, a tangent modulus of about 165,000 to about 225,000, and a melting point of about 150 to about 190 F.

7. The composition of Claim 1, wherein the polymer is derived from monomers of lactide selected from the group consisting of L-lactide, D-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof.

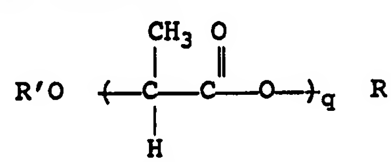
8. The composition of Claim 1, wherein the composition comprises from about 2 to about 60 weight percent plasticizer.

9. The composition of Claim 1, comprising additional plasticizer dispersed within the composition that is selected from the group consisting of lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, oligomers of lactic acid, oligomers of lactide, and mixtures thereof.

10. A process for producing a biodegradable composition useful as a replacement for thermoplastic polymer compositions comprising:

a. providing a poly(lactic acid); and

b. incorporating plasticizer into the poly(lactic acid) selected from one or more derivatives of an oligomer of lactic acid, defined by the formula:



where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated,

where R′ = H, alkyl, aryl, alkylaryl or acetyl, and R′ is saturated,
where R and R′ cannot both be H,
and where q is an integer: $2 \leq q \leq 75$.

11. The process of Claim 10, whereby q is an integer: $2 \leq q \leq 10$.

12. The process of Claim 10, wherein the plasticizer is added in an amount to obtain a plasticizer content between about 2 to about 60 weight percent.

13. The process of Claim 10, comprising incorporating additional plasticizer selected from the group consisting of lactic acid, L-lactide, D-lactide, meso D,L-lactide, racemic D,L-lactide, oligomers of lactic acid, oligomers of lactide, and mixtures thereof.

14. The process of Claim 12, comprising incorporating the plasticizer in a manner adapted to obtain an intimate dispersion of the plasticizer within the polymer.

15. The process of Claim 14, extruding the plasticized poly(lactic acid) as a blown film.

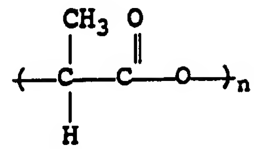
16. The process of Claim 15, comprising maintaining the intimate dispersion of plasticizer during the extrusion of the blown film.

17. The process of Claim 14, comprising processing the composition into a final product in a manner adapted to retain the plasticizer as an intimate dispersion within the polymer.

18. The process of Claim 14, comprising quenching the composition at a rate adapted to retain the plasticizer as an intimate dispersion within the polymer.

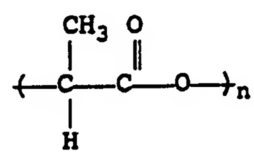
19. The process of Claim 10, comprising melt fabricating and quenching the composition at a rate adapted to retain the monomer as an intimate dispersion within the polymer.

20. The process of Claim 15, comprising: providing the poly(lactic acid) in step (a) having the repeating units,



wherein n is the number of repeating units and n is an integer, $150 \leq n \leq 20{,}000$; and plasticizing the poly(lactic acid) to obtain a composition which when unoriented has a tensile strength of about 1,200 to about 4,000 psi, an elongation to failure of about 100 to about 800 percent, and a tangent modulus of about 20,000 to about 75,000 psi.

21. The process of Claim 15, comprising: providing the poly(lactic acid) in step (a) having the repeating units,



wherein n is the number of repeating units and n is an integer, $150 \leq n \leq 20{,}000$; and plasticizing the poly(lactic acid) to obtain a composition which when unoriented has a tensile strength of about 4,500 to about 10,000 psi, an elongation to failure of about 100 to about 600 percent, a tangent modulus of about 165,000 to about 225,000, and a melting point of about 150 to about 190 F.

22. A process for incorporating plasticizer into poly(lactic acid) to obtain a blended composition comprising:

a. melt blending with a poly(lactic acid), a first plasticizer selected from the group consisting of oligomers of lactic acid, oligomers of lactide, and mixtures thereof at a first temperature;

b. melt blending with the obtained blend a second plasticizer selected from the group consisting of lactic acid, L-lactide, D-lactide, meso D,L-lactide, racemic D,L-lactide, and

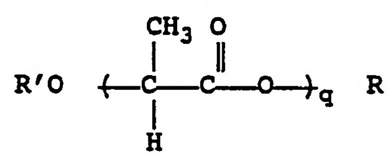
mixtures thereof, at a second temperature lower than the first temperature; and

whereby an intimate dispersion of the plasticizers is obtained.

23. The process of Claim 22, comprising quenching the composition at a rate adapted to retain the plasticizer as an intimate dispersion within the polymer.

24. A process for incorporating plasticizer into poly(lactic acid) to obtain a blended composition comprising:

a. melt blending with a poly(lactic acid), a first plasticizer selected from the group consisting of one or more derivatives of an oligomer of lactic acid, defined by the formula:



where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated,

where R′ = H, alkyl, aryl, alkylaryl or acetyl, and R′ is saturated,

where R and R′ cannot both be H,

where q is an integer: $2 \leq q \leq 75$, at a first temperature; and

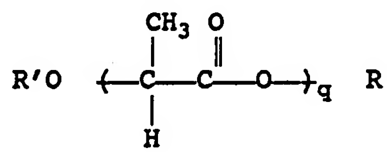
b. melt blending with the obtained blend a second plasticizer selected from the group consisting of lactic acid, L-lactide, D-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof, at a second temperature lower than the first temperature; and

whereby an intimate dispersion of the plasticizers is obtained.

25. The process of Claim 24, wherein q is an integer: $2 \leq q \leq 10$.

26. The process of Claim 24, comprising quenching the composition at a rate adapted to retain the plasticizer as an intimate dispersion within the polymer.

27. An environmentally decomposable polymeric composition suitable for use as a substitute for crystal polystyrene comprising a poly(lactic acid), where the repeating unit is an L- or D-enantiomer and there is a preponderance of either enantiomer, having intimately dispersed therein greater than about 0.1 weight percent of a plasticizer selected from the group consisting of one or more derivatives of an oligomer of lactic acid, defined by the formula:



where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated,
where R′ = H, alkyl, aryl, alkylaryl or acetyl, and R′ is saturated,
where R and R′ cannot both be H,
and where q is an integer: $2 \leq q \leq 75$; wherein the unoriented composition has a tensile strength of at least about 5,000 psi, a tangent modulus of at least about 200,000 psi, and is substantially colorless.

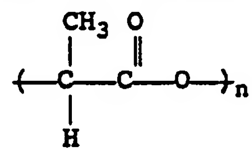
28. The composition of Claim 27, wherein the plasticizer comprises:

a. a second plasticizer selected from the group consisting of oligomers of lactic acid, oligomers of lactide, and mixtures thereof, wherein the oligomers of lactic acid and oligomers of lactide have a number average molecular weight below about 5,400; and/or

b. a third plasticizer selected from the group consisting of lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof.

29. The composition of Claim 27, wherein the composition is form stable above about 70 C.

30. The composition of Claims 27 or 28 wherein the polylactide is defined by the formula:



where n is an integer between about 450 and about 10,000, where the repeating unit is an L-or D-enantiomer and there is a preponderance of either enantiomer.

31. The composition of Claim 30, wherein the ratio of L-enantiomer to D-enantiomer is between about 1/99 and about 99/1.

32. The composition of Claim 30, wherein the ratio of L-enantiomer to D-enantiomer is between about 2.5/97.5 and 7.5/92.5, or between about 92.5/7.5 and 97.5/2.5.

33. The composition of Claim 30, comprising a nucleating agent selected from the group consisting of lactate salts, benzoate salts, poly(L-lactide), poly(D-lactide), and mixtures thereof.

34. The composition of Claim 30, comprising a plasticizer present in an amount effective to provide substantial transparency.

35. The composition of Claim 28, wherein the oligomers of lactic acid, and the oligomers of lactide have a number average molecular weight below about 720.

36. The composition of Claim 30, wherein the plasticizer is present in an amount between about 0.1 and about 10 weight percent.

37. The composition of Claim 36, wherein the plasticizer is present in an amount above about 5 weight percent.

38. An environmentally decomposable polymeric composition suitable for use as a substitute for crystal polystyrene comprising a physical mixture of:

a. a first poly(lactic acid) having a preponderance of either D- or L-enantiomers;

b. a second poly(lactic acid) selected from the group consisting of poly(D-lactic acid) or a poly(L-lactic acid), wherein the weight percent ratio of the first poly(lactic acid) to the second poly(lactic acid) is between about 1/99 and 99/1; and

c. greater than about 0.1 weight percent of plasticizer selected from the group consisting of one or more derivatives of an oligomer of lactic acid, defined by the formula:

$$R'O \left(-\underset{\displaystyle H}{\overset{\displaystyle CH_3}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-O- \right)_q R$$

where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated,

where R' = H, alkyl, aryl, alkylaryl or acetyl, and R' is saturated,

where R and R' cannot both be H,

and where q is an integer: $2 \leq q \leq 75$,

wherein the plasticizer is intimately dispersed within the poly(lactic acid)s, and the unoriented composition has a tensile strength of at least 5,000 psi and a tangent modulus of at least 200,000 psi.

39. The composition of Claim 38, wherein the plasticizer comprises:

a. a second plasticizer selected from the group consisting of oligomers of lactic acid, oligomers of lactide, and mixtures thereof, wherein the oligomers of lactic acid and oligomers of lactide have a number average molecular weight below about 5,400; and/or

b. a third plasticizer selected from the group consisting of lactic acid, D-lactide, L-

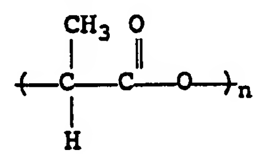
lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof.

40. The composition of Claim 39, wherein the composition is form stable above about 70 C.

41. The composition of Claim 39, wherein the ratio of the first poly(lactic acid) to the second poly(lactic acid) is between about 98/2 and about 75/25.

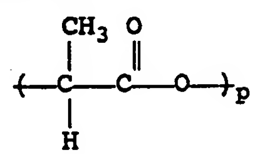
42. The composition of Claim 39, wherein:

a. the first poly(lactic acid) is defined by the formula:



where n is an integer between about 450 and about 10,000; and

b. the second poly(lactic acid) is defined by the formula:



where p is an integer between about 450 and about 10,000.

43. The composition of Claim 42, wherein the plasticizer is present in an amount between about 0.1 and about 10 weight percent.

44. The composition of Claim 43, wherein the plasticizer is present in an amount greater than about 5 weight percent.

45. The composition of Claim 42, comprising a nucleating agent selected from the group consisting of lactate salts, benzoate salts, poly(L-lactide), poly(D-lactide), and mixtures thereof.

46. The composition of Claim 43, comprising: a film or sheet product; the oriented and annealed product having a tensile strength in excess of 7,500, a tangent modulus in excess of 350,000, and having dimensional heat stability at temperatures above about 70 C.

47. The product of Claim 46, wherein the product is biaxially oriented.

48. The composition of Claim 46, wherein the ratio of the first poly(lactic acid) to the second poly(lactic acid) is between about 98/2 and about 75/25.

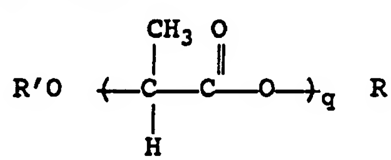
49. The composition of Claims 27, 28, 38, 39, 42, or 46 processed into a foam product.

50. The compositions of Claims 27, 28, 38, 39, 42, and 46 processed into a product wherein: the poly(lactic acid)s have a number average molecular weight, M_n, between about 50,000 and 400,000; and wherein the product has the physical properties of: a tensile strength of at least about 7500 psi; a tangent modulus of at least 350,000, form stability above about 70 C, and being substantially colorless after processing into a product.

51. A process for the manufacture of an environmentally decomposable film or sheet forming polymeric composition suitable for use as a substitute for crystal polystyrene comprising:

a. providing a poly(lactic acid) having D- and L-enantiomers with a preponderance of either the D-, or L-enantiomer;

b. incorporating plasticizer selected from the group consisting of one or more derivatives of an oligomer of lactic acid, defined by the formula:



where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated,

where R′ = H, alkyl, aryl, alkylaryl or acetyl, and R′ is saturated,

where R and R′ cannot both be H,

and where q is an integer: $2 \leq q \leq 75$, the unoriented composition having a tensile strength of at least 5,000 psi and a tangent modulus of at least 200,000 psi, is substantially colorless, and wherein the plasticizer is intimately blended with the composition.

52. The process of Claim 51, wherein the polylactide has a ratio of L-enantiomer to D-enantiomer of between about 1/99 and 99/1.

53. The process of Claim 51, wherein the polylactide has a ratio of L-enantiomer to D-enantiomer of between about 2.5/97.5 and 7.5/92.5 or between about 92.5/7.5 and 97.5/2.5.

54. The process of Claim 51, wherein the plasticizer is added in an amount effective to prevent degradation and discoloration of the film or sheet prior to further processing.

55. The process of Claim 51, wherein the plasticizer comprises:

a. a second plasticizer selected from the group consisting of oligomers of lactic acid, oligomers of lactide, and mixtures thereof, having a number average molecular weight below about 5,400; and/or

b. a third plasticizer selected from the group consisting of lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof.

56. The process of Claim 51 or 55, wherein the polymeric composition is extruded into a film or sheet and physically treated by orientation and/or annealing to provide a polymeric film or sheet having a tensile strength of at least 7,500 psi and a tangent modulus of at least 350,000 psi.

57. The process of Claim 51 or 55, whereby the film or sheet is biaxially oriented.

58. The process of Claim 51 or 55, whereby the film or sheet is oriented and heat-set to retain the orientation.

59. The process of Claim 51 or 55, wherein step (a) of providing a poly(lactic acid) comprises:

1. providing a first poly(lactic acid) having a preponderance of either D- or L-enantiomers;

2. providing a second poly(lactic acid) selected from the group consisting of poly(D-lactic acid) or a poly(L-lactic acid), wherein the weight percent ratio of the first poly(lactic acid) to the second poly(lactic acid) is betwee about 1/99 and 99/1.

60. The process of Claim 59, wherein plasticizer is added in an amount between about 0.1 and about 10 weight percent.

61. The process of Claim 59, wherein the step of incorporating plasticizer comprises:

a. incorporating a second plasticizer selected from the group consisting of oligomers of lactic acid, oligomers of lactide, and mixtures thereof, wherein the oligomers of lactic acid and oligomers of lactide have a number average molecular weight below about 5,400; and/or

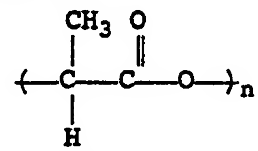
b. incorporating a third plasticizer selected from the group consisting of lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof.

62. The process of Claim 59, wherein the composition is form stable above about 70 C.

63. The process of Claim 59, wherein the ratio of the first poly(lactic acid) to the second poly(lactic acid) is between about 98/2 and about 75/25.

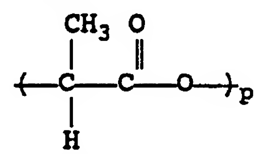
64. The process of Claim 59, wherein:

a. the first poly(lactic acid) is defined by the formula:



where n is an integer between about 450 and about 10,000; and

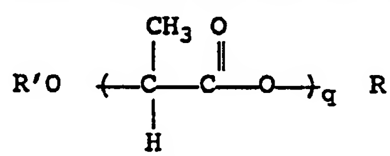
b. the second poly(lactic acid) is defined by the formula:



where p is an integer between about 450 and about 10,000.

65. The process of Claim 55, wherein the plasticizer is sequentially added by melt blending:

a. one or more derivatives of an oligomer of lactic acid defined by the formula:



where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated,

where R′ = H, alkyl, aryl, alkylaryl or acetyl, and R′ is saturated,

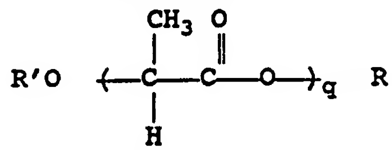
where R and R′ cannot both be H,

and where q is an integer: $2 \leq q \leq 75$, whereby the blending is at a first temperature; and

b. a second plasticizer selected from the group consisting of lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof, whereby the blending is at a second temperature lower than the first temperature.

66. The process of Claim 61, wherein the plasticizer is sequentially added by melt blending:

a. one or more derivatives of an oligomer of lactic acid defined by the formula:



where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated,
where R′ = H, alkyl, aryl, alkylaryl or acetyl, and R′ is saturated,
where R and R′ cannot both be H,
and where q is an integer: $2 \leq q \leq 75$, whereby the blending is at a first temperature; and

b. a second plasticizer selected from the group consisting of lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof, whereby the blending is at a second temperature lower than the first temperature.

67. The process of Claim 58, wherein the plasticizer is sequentially added by melt blending:

a. a first plasticizer selected from the group consisting of oligomers of lactic acid, oligomers of lactide, and mixtures thereof, whereby the blending is at a first temperature; and

b. a second plasticizer selected from the group consisting of lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof, whereby the blending is at a second temperature lower than the first temperature.

68. The process of Claim 61, wherein the plasticizer is sequentially added by melt blending:

a. a first plasticizer selected from the group consisting of oligomers of lactic acid, oligomers of lactide, and mixtures thereof,

whereby the blending is at a first temperature; and

b. a second plasticizer selected from the group consisting of lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof, whereby the blending is at a second temperature lower than the first temperature.

69. The process of Claim 55, wherein the plasticizer added is selected to control the rate of environmental decomposition.

70. The process of Claim 55, wherein the provided polymer has a polydispersity, M_w/M_n, of between about 1.8 and about 2.6.

71. The process of Claim 55, wherein the polymer has a viscosity of less than about 100,000 poise.

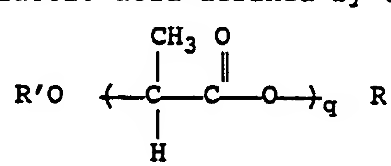
72. The process of Claim 55, wherein the annealing is carried out at a temperature between about 80 C and about 140 C until the film or sheet has form stability above 70 C.

73. An environmentally degradable composition comprising melt blends of a physical mixture of:

a. a poly(lactic acid);

b. a polymer selected from the group consisting of a poly(ethylene terephthalate), a polymer or copolymer of styrene, ethylene, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof; and

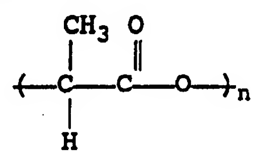
c. plasticizer selected from the group consisting of one or more derivatives of an oligomer of lactic acid defined by the formula:



where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated,
where R' = H, alkyl, aryl, alkylaryl or acetyl, and R' is saturated,
where R and R' cannot both be H,
and where q is an integer: $2 \leq q \leq 75$, wherein the oligomers have a number average molecular weight below about 5,400; and wherein the plasticizer is intimately dispersed within at least the poly(lactic acid).

74. The composition of Claim 73, wherein q is an integer: $2 \leq q \leq 10$.

75. The composition of Claim 73, wherein one or more poly(lactic acid)s have the structure:



where n is an integer between 75 and 10,000.

76. The composition of Claim 73, wherein the plasticizer comprises:

a. a second plasticizer selected from the group consisting of oligomers of lactic acid, oligomers of lactide, and mixtures thereof, wherein the oligomers have a number average molecular weight below about 5,400; and/or

b. a third plasticizer selected from the group consisting of lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof.

77. The composition of Claim 76, comprising a plasticizer present in an amount effective to provide compatibilization of the melt blend components.

78. The composition of Claim 76, comprising a plasticizer present in an amount effective to regulate sensitivity to degradation by moisture.

79. The composition of Claim 73, in which the plasticizer is added in an amount between about 0.1 and about 10 weight percent.

80. The composition of Claim 73, comprising between about 1 to about 99 weight percent poly(lactic acid).

81. The composition of Claim 73, comprising between about 5 to 50 weight percent poly(lactic acid).

82. The composition of Claim 73, comprising between about 10 to 20 weight percent poly(lactic acid).

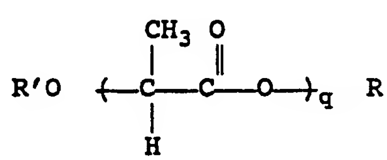
83. The composition of Claim 73, comprising between about 80 to 99 weight percent poly(lactic acid).

84. A process for producing the composition of Claim 73, comprising:

a. providing a poly(lactic acid);

b. selecting a polymer from the group consisting of poly(ethylene terephthalate), a polymer or copolymer of styrene, ethylene, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof;

c. providing a plasticizer selected from the group consisting of one or more derivatives of an oligomer of lactic acid defined by the formula:



where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated,
where R′ = H, alkyl, aryl, alkylaryl or acetyl, and R′ is saturated,
where R and R′ cannot both be H,
and where q is an integer: $2 \leq q \leq 75$; and

d. blending the polymers of steps (a) and (b) with the plasticizer of step (c).

85. The process of Claim 84, comprising providing a plasticizer present in an amount effective to provide compatibilization of the melt blend components.

86. The process of Claim 84, comprising providing a plasticizer present in an amount effective to regulate its sensitivity to degradation by moisture.

87. The process of Claim 84, comprising:

a. providing a second plasticizer selected from the group consisting of an oligomer of lactide, or an oligomer of lactic acid; and/or

b. providing a third plasticizer selected from the group consisting of lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof.

88. The process of Claim 87, wherein the oligomers have a number average molecular weight below about 720.

89. The process of Claim 73, wherein q is an integer: $2 \leq q \leq 10$.

90. The process of Claim 84, in which the plasticizer is added in an amount between about 0.1 and about 10 weight percent.

91. The process of Claim 84, whereby the blending is achieved by melt blending.

92. The process of Claim 84, whereby the blending is achieved by mill roll blending.

93. A process for producing an environmentally degradable composition comprising:

a. providing lactide monomer selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide and mixtures thereof;

b. selecting a polymer from the group consisting of poly(ethylene terephthalate), a polymer or copolymer of styrene, ethylene, propylene, vinyl chloride, vinyl acetate, alkyl

methacrylate, alkyl acrylate, and physical mixtures thereof;

c. mixing and heating the lactide selected in (a) and the polymer selected in (b) at conditions adapted to melt the lactide and at least partially dissolve the polymer;

d. polymerizing the lactide in the mixture of step (c) to obtain a blend of polylactide and polymer; and

e. adding to the blend after polymerization a plasticizer selected from the group consisting of one or more derivatives of an oligomer of lactic acid defined by the formula:

$$R'O\left(-\underset{\displaystyle H}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle O}{\overset{\|}{C}}-O-\right)_q R$$

where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated,
where R′ = H, alkyl, aryl, alkylaryl or acetyl, and R′ is saturated,
where R and R′ cannot both be H,
and where q is an integer: $2 \leq q \leq 75$, whereby the plasticizer is intimately dispersed within at least the poly(lactic acid).

94. The process of Claim 93, comprising the additional step:

f. forming the blend into a self supporting structure.

95. The process of Claim 93, comprising monitoring the amount of monomer remaining and controlling the polymerization of step (d) to obtain a blend containing residual monomer.

96. The composition obtained from the process of Claim 93.

97. The process of Claim 93, comprising adding a plasticizer in an amount effective to provide compatibilization of the melt blend components.

98. The process of Claim 93, comprising adding a plasticizer in an amount effective to regulate its sensitivity to degradation by moisture.

99. The process of Claim 93, comprising providing a plasticizer selected from the group consisting of an oligomer of lactide, or an oligomer of lactic acid having a number average molecular weight below about 720.

100. The process of Claim 93, wherein q is an integer: $2 \leq q \leq 10$.

101. The process of Claim 93, comprising:

a. providing a second plasticizer selected from the group consisting of oligomers of lactic acid, oligomers of lactide, and mixtures thereof, wherein the oligomers have a number average molecular weight below about 5,400; and/or

b. providing a third plasticizer selected from the group consisting of lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof.

102. The process of Claim 100, in which the plasticizer is added in an amount between about 0.1 and about 10 weight percent.

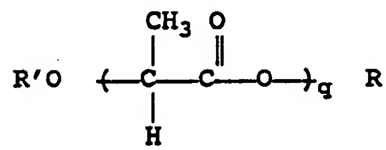
103. The composition obtained from the process of Claim 93.

104. An environmentally degradable composition comprising: blends of a physical mixture of:

a. a poly(lactic acid);

b. an elastomeric blend compatible polymer that provides an improved impact resistant composition, and the elastomeric blend compatible polymer is discrete and intimately bound; and

c. a plasticizer selected from the group consisting of one or more derivatives of an oligomer of lactic acid defined by the formula:



where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated,
where R′ = H, alkyl, aryl, alkylaryl or acetyl, and R′ is saturated,
where R and R′ cannot both be H,
and where q is an integer: $2 \leq q \leq 75$, and wherein the plasticizer is intimately dispersed within at least the poly(lactic acid).

105. The composition of Claim 104, wherein the plasticizer is present in an amount effective to provide desired stiffness.

106. The composition of Claim 104, comprising plasticizer present in an amount to provide more intimate compatibility of the poly(lactic acid) and the elastomeric impact modifier.

107. The composition of Claim 104, wherein the plasticizer comprises:

a. a second plasticizer selected from the group consisting of oligomers of lactic acid, oligomers of lactide, and mixtures thereof, wherein the oligomers have a number average molecular weight below about 5,400; and/or

b. a third plasticizer selected from the group consisting of lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof.

108. The composition of Claim 107, wherein the oligomers have a number average molecular weight below about 720.

109. The composition of Claim 104, wherein q is an integer: $2 \leq q \leq 10$.

110. The composition of Claim 104, comprising between about 0.1 to about 10 weight percent plasticizer.

111. The composition of Claim 104, comprising between about 1 to about 99 weight percent poly(lactic acid).

112. The composition of Claim 104, wherein the elastomeric blend compatible polymer is selected from the group consisting of polyisoprene (gutta percha), styrene-isoprene-styrene block copolymers, acrylonitrile-butadiene-styrene block copolymers, styrene-ethylene-styrene block copolymers, propylene-ethylene-propylene block copolymers, propylene-isoprene-propylene block copolymers and mixtures thereof.

113. The process of Claim 104, whereby the elastomeric blend compatible polymer is selected from polyurethanes that are not significantly water swellable or water soluble.

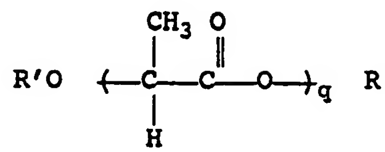
114. The composition of Claim 104, wherein the blend compatible polymer is a segmented polymer.

115. The composition of Claim 114, comprising an elastomeric blend compatible polymer selected from the group consisting of a block copolymer of hard crystalline segments of poly(butylene terephthalate) and soft long chain segments of poly(ether glycols), natural rubber, styrene-butadiene copolymers, and mixtures thereof.

116. A process for producing the composition of Claim 104, comprising:

a. providing a poly(lactic acid);

b. providing a plasticizer selected from the group consisting of one or more derivatives of an oligomer of lactic acid defined by the formula:



where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated,
where R′ = H, alkyl, aryl, alkylaryl or acetyl, and R′ is saturated,
where R and R′ cannot both be H,
and where q is an integer: $2 \le q \le 75$;

c. providing an elastomeric blend compatible polymer that provides an improved impact resistant composition, and the elastomeric blend compatible polymer is discrete and intimately bound; and

d. blending the polymers of steps (a) and (c) with the plasticizer of step b.

117. The process of Claim 104, comprising: providing:

a. a second plasticizer selected from the group consisting of oligomers of lactic acid, oligomers of lactide, and mixtures thereof, having a number average molecular weight below about 5,400; and/or

b. a third plasticizer selected from the group consisting of lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof.

118. The process of Claim 116, providing oligomers having a number average molecular weight below about 720.

119. The process of Claim 117, wherein the first plasticizer is incorporated at a first temperature, and the second plasticizer is incorporated at a second temperature lower than the first temperature.

120. The process of Claim 116, wherein:

1. the plasticizer provided in step (b) is blended in step (d) at a first temperature; and

2. a second plasticizer selected from the group consisting of lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof, is blended at a second temperature lower than the first temperature.

121. The process of Claim 116, in which the plasticizer is added in an amount between about 0.10 and about 10 weight percent.

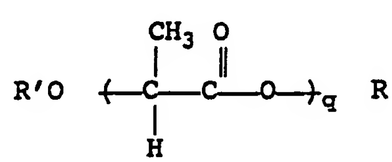
122. A process for producing the composition of Claim 104, comprising:

a. mixing one or more lactides selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide and mixtures thereof with an elastomeric blend compatible polymer that provides an improved impact resistant composition;

b. heating and dissolving the blend compatible polymer in the lactide(s) of step (a) to form a solution;

c. polymerizing the lactide(s) in the solution; and

d. incorporating plasticizer in the composition, whereby the plasticizer is intimately dispersed within at least the poly(lactic acid) and the plasticizer is selected from the group consisting of one or more derivatives of an oligomer of lactic acid defined by the formula:



where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated,

where R′ = H, alkyl, aryl, alkylaryl or acetyl, and R′ is saturated,
where R and R′ cannot both be H,
and where q is an integer: $2 \leq q \leq 75$.

123. The process of Claim 122, comprising the step of fabricating the composition into useful forms by melt fabrication.

124. The process of Claim 122, comprising selecting a blend compatible polymer that comprises a segmented polyester.

125. The Process of Claim 122, incorporating a second plasticizer selected from the group consisting of lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, oligomers of lactic acid, oligomers of lactide, and mixtures thereof, wherein the oligomers have a number average molecular weight below about 5,400.

126. A degradable composition comprising: blends of a physical mixture of:

a. a poly(lactic acid); and

b. an elastomeric blend compatible polymer that provides improved impact resistance to the poly(lactic acid), wherein the polymer is selected from the group consisting of polyisoprene (gutta percha), styrene-isoprene-styrene block copolymers, acrylonitrile-butadiene-styrene block copolymers, styrene-ethylene-styrene block copolymers, propylene-ethylene-propylene block copolymers, propylene-isoprene-propylene block copolymers and mixtures thereof.

127. A process for producing the composition of Claim 126, comprising:

a. providing a poly(lactic acid);

b. selecting a blend compatible polymer that provides improved impact resistance to the poly(lactic acid) from the group consisting of polyisoprene (gutta percha), styrene-isoprene-

styrene block copolymers, acrylonitrile-butadiene-styrene block copolymers, styrene-ethylene-styrene block copolymers, propylene-ethylene-propylene block copolymers, propylene-isoprene-propylene block copolymers and mixtures thereof; and

c. blending the polymers of steps (a) and (b).

128. A process for producing the composition of Claim 126, comprising:

a. mixing one or more lactides selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide and mixtures thereof with a blend compatible polymer that provides improved impact resistance to the composition, wherein the blend compatible polymer is selected from the group consisting of polyisoprene (gutta percha), styrene-isoprene-styrene block copolymers, acrylonitrile-butadiene-styrene block copolymers, styrene-ethylene-styrene block copolymers, propylene-ethylene-propylene block copolymers, propylene-isoprene-propylene block copolymers and mixtures thereof;

b. heating and dissolving the blend compatible polymer in the lactide(s) of step a to form a solution; and

c. polymerizing the lactide(s) in the solution.

129. An environmentally degradable composition comprising: blends of a physical mixture f:

a. a poly(lactic acid);

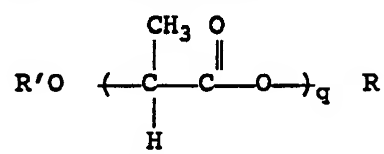
b. an elastomeric blend compatible polymer that provides an improved impact resistant composition, selected from the group consisting of polyisoprene (gutta percha), styrene-isoprene-styrene block copolymers,

acrylonitrile-butadiene-styrene block copolymers, styrene-ethylene-styrene block copolymers, propylene-ethylene-propylene block copolymers, propylene-isoprene-propylene block copolymers and mixtures thereof; and

c. a plasticizer selected from the group consisting of lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, oligomers of lactic acid, oligomers of lactide, and mixtures thereof, wherein the oligomers have a number average molecular weight below about 5,400, and wherein the plasticizer is intimately dispersed within at least the poly(lactic acid).

130. The composition of Claim 129, comprising:

a. a first plasticizer selected from the group consisting of one or more derivatives of an oligomer of lactic acid defined by the formula:



where R = H, alkyl, aryl, alkylaryl or acetyl, and R is saturated,

where R′ = H, alkyl, aryl, alkylaryl or acetyl, and R′ is saturated,

where R and R′ cannot both be H,

and where q is an integer: $2 \leq q \leq 75$; and

b. a second plasticizer selected from the group consisting of lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof.

131. The composition of Claim 129, comprising between about 0.1 to about 10 weight percent plasticizer.

132. The composition of Claim 129, comprising between about 1 to about 99 weight percent poly(lactic acid).

133. A process for producing the composition of Claim 129, comprising:

a. providing a poly(lactic acid);

b. providing a plasticizer selected from the group consisting of lactic acid, D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, oligomers of lactic acid, oligomers of lactide, and mixtures thereof, wherein the oligomers have a number average molecular weight below about 5,400;

c. providing an elastomeric blend compatible polymer that provides an improved impact resistant composition, and the elastomeric blend compatible polymer is discrete and intimately bound; and

d. blending the polymers of steps (a) and (c) with the plasticizer of step b.

134. The process of Claim 133, providing oligomers having a number average molecular weight below about 720.

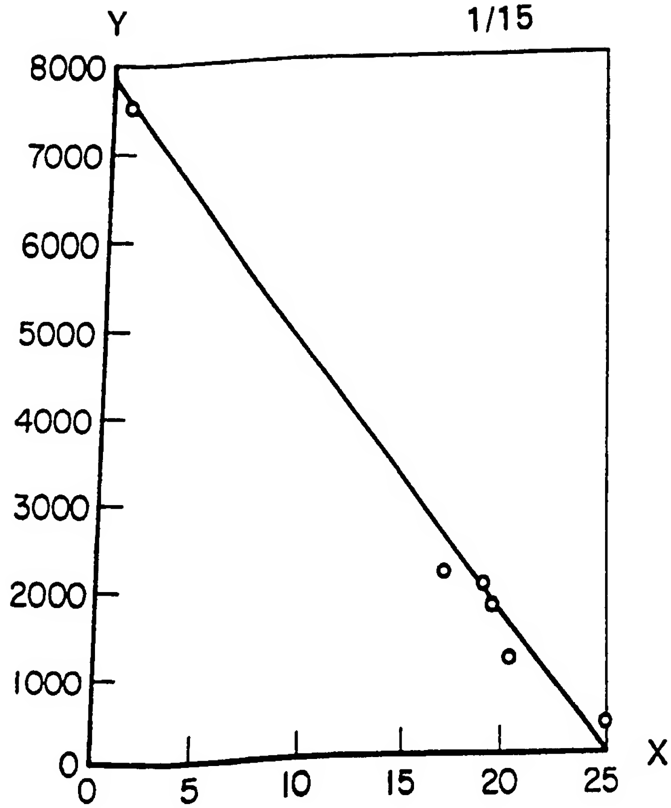
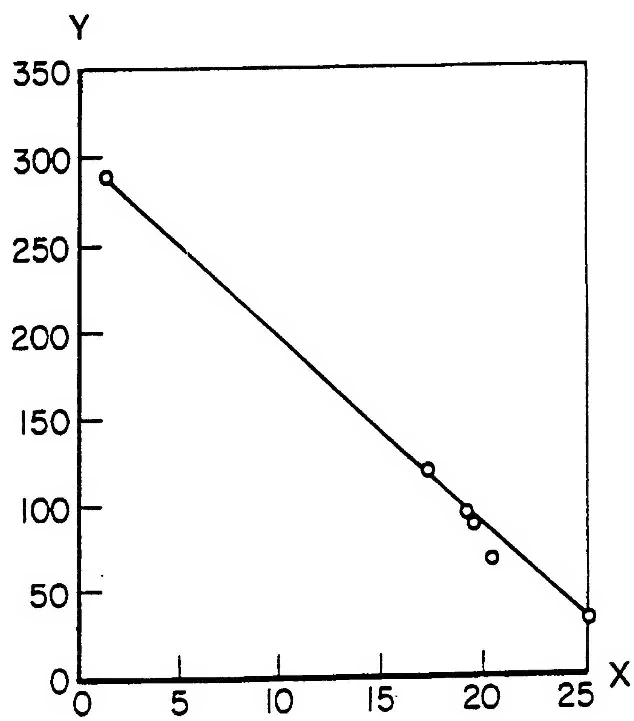

Y
8000
7000
6000
5000
4000
3000
2000
1000
0
0
5
10
15
20
25
X

FIG. 1

FIG. 2


Y
350
300
250
200
150
100
50
0
0
5
10
15
20
25
X

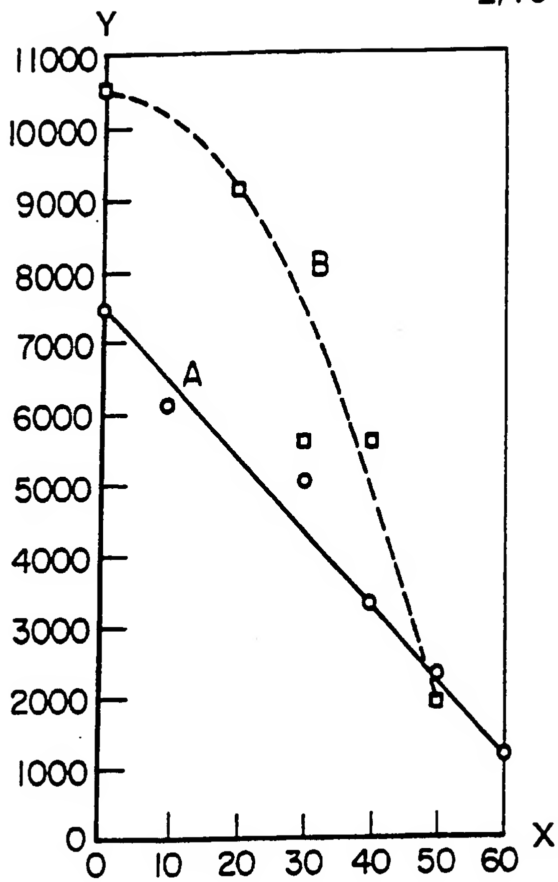

Y
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0 10 20 30 40 50 60
X
A
B

FIG. 3

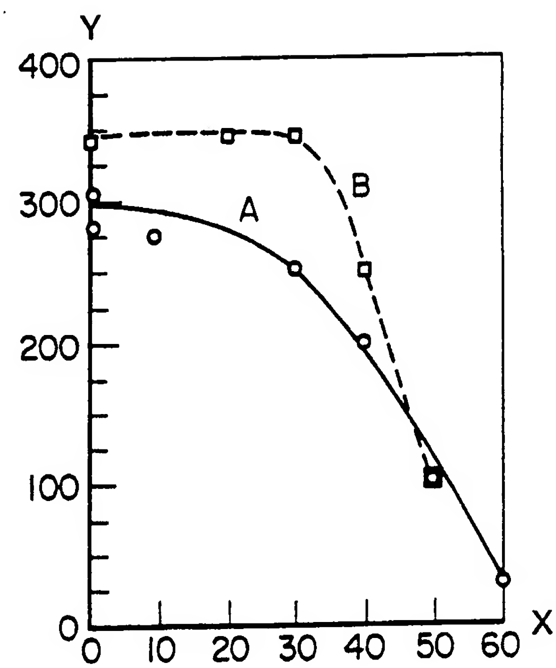

Y
400
300
200
100
0
0 10 20 30 40 50 60
X
A
B

FIG. 4

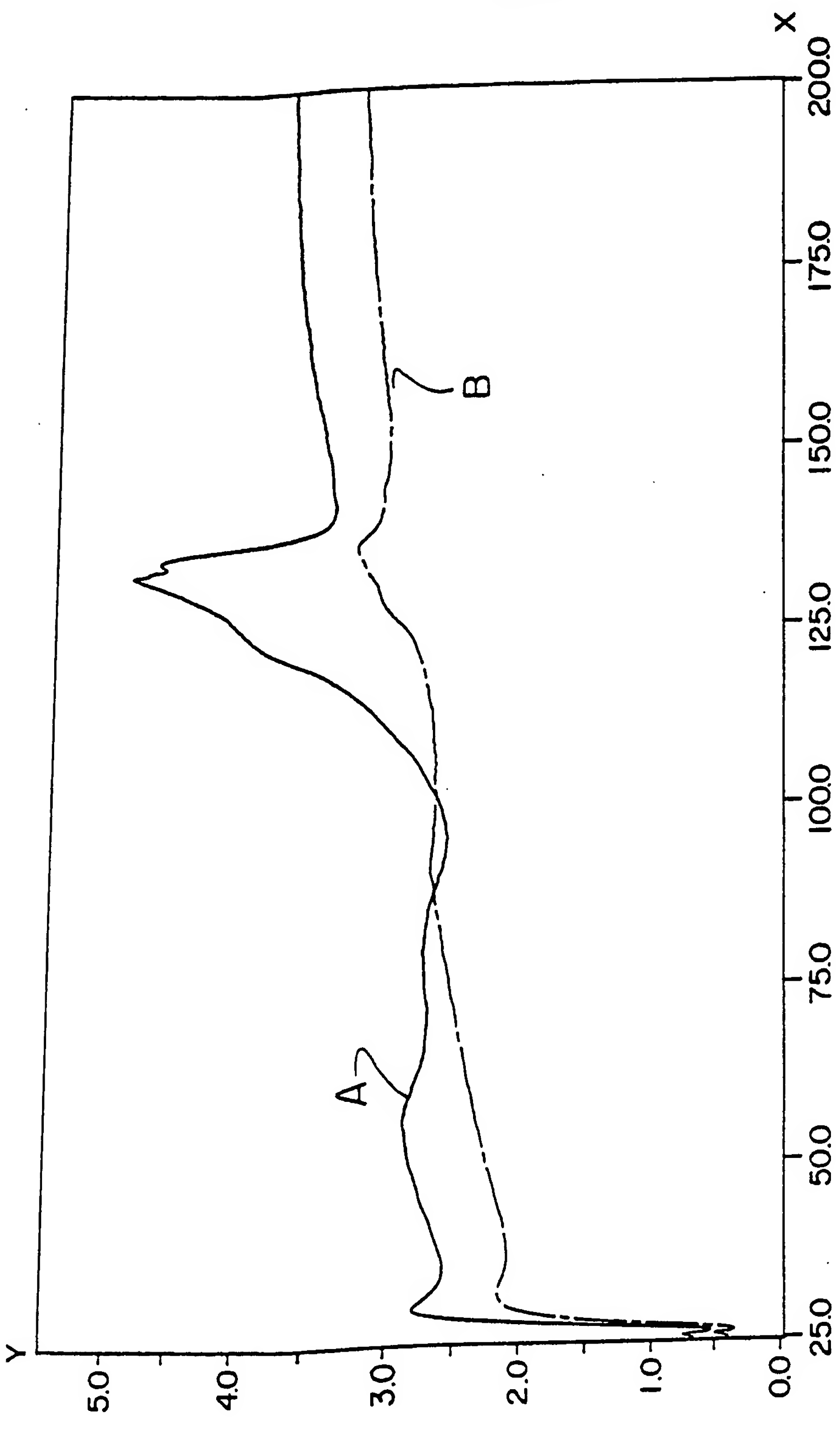


FIG. 5

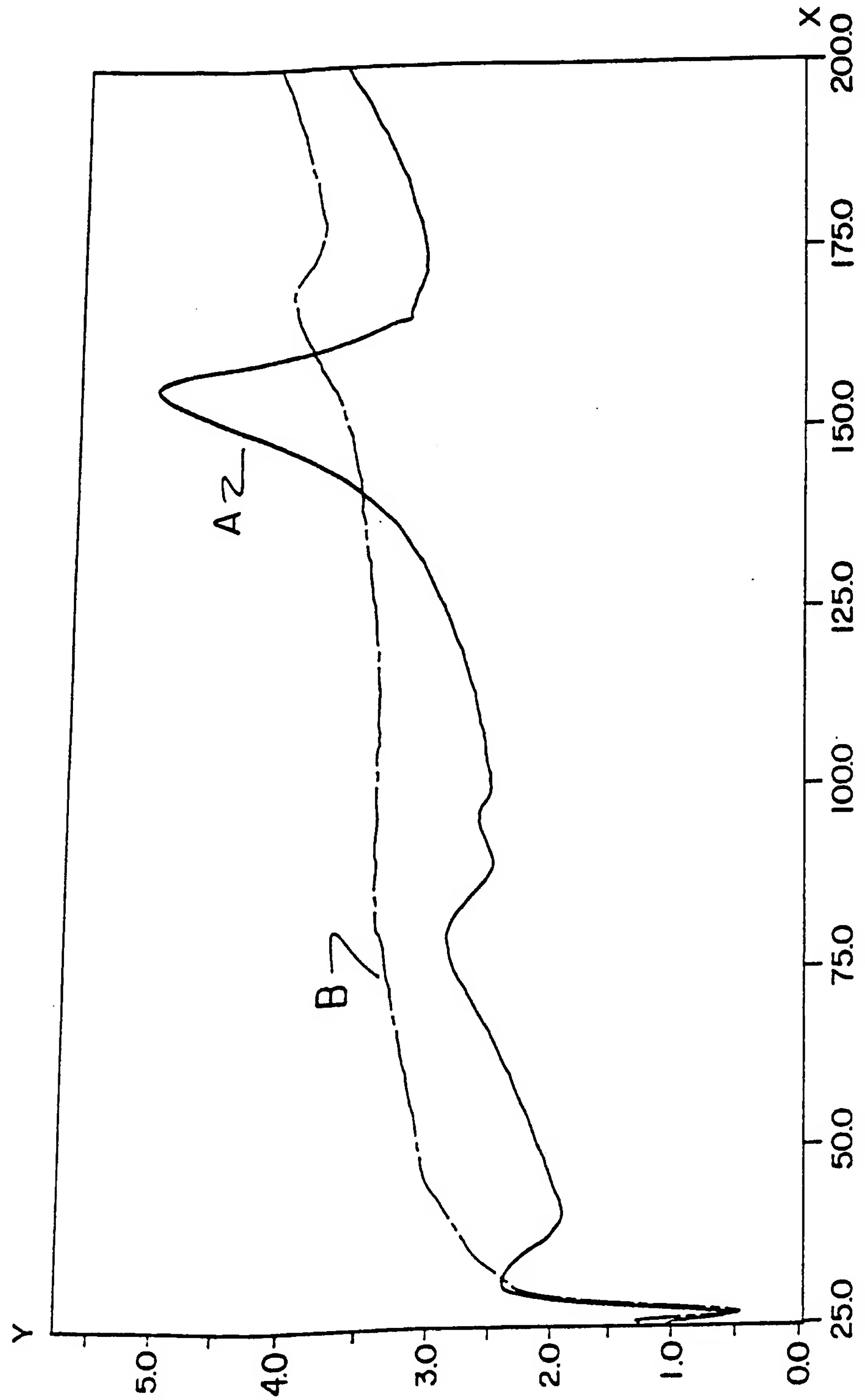


FIG. 6

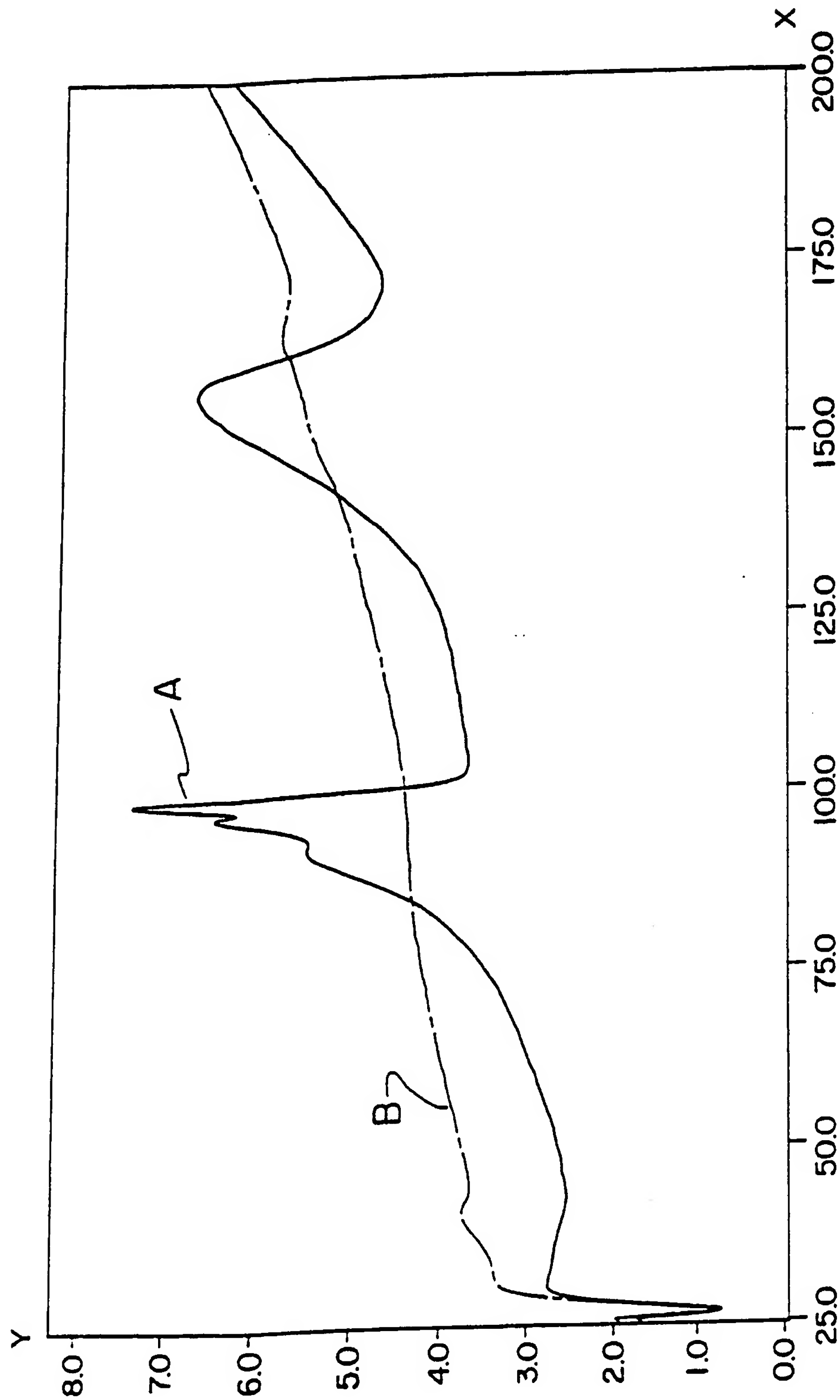

Y
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
X
25.0
50.0
75.0
100.0
125.0
150.0
175.0
200.0
A
B

FIG. 7

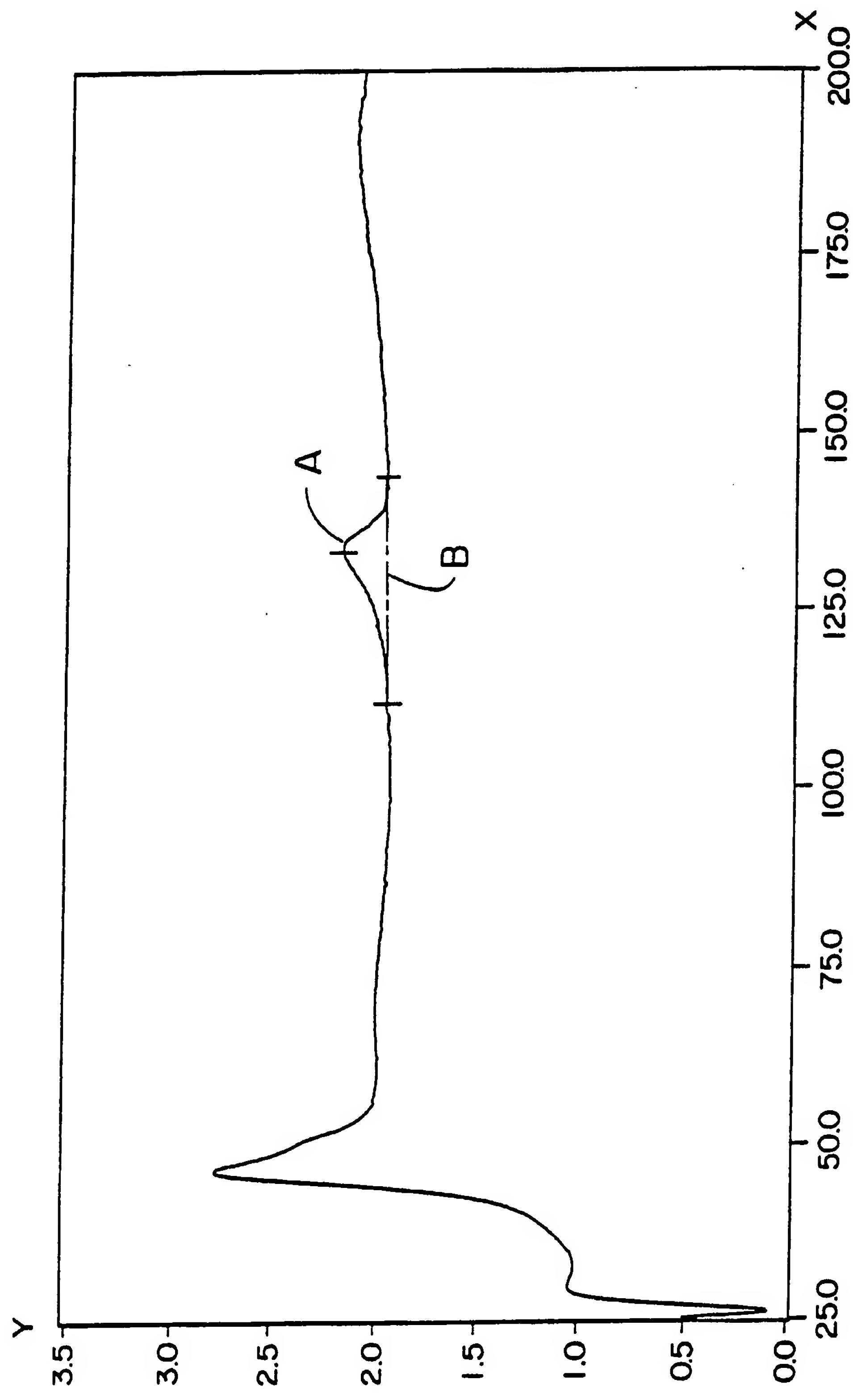


FIG. 8

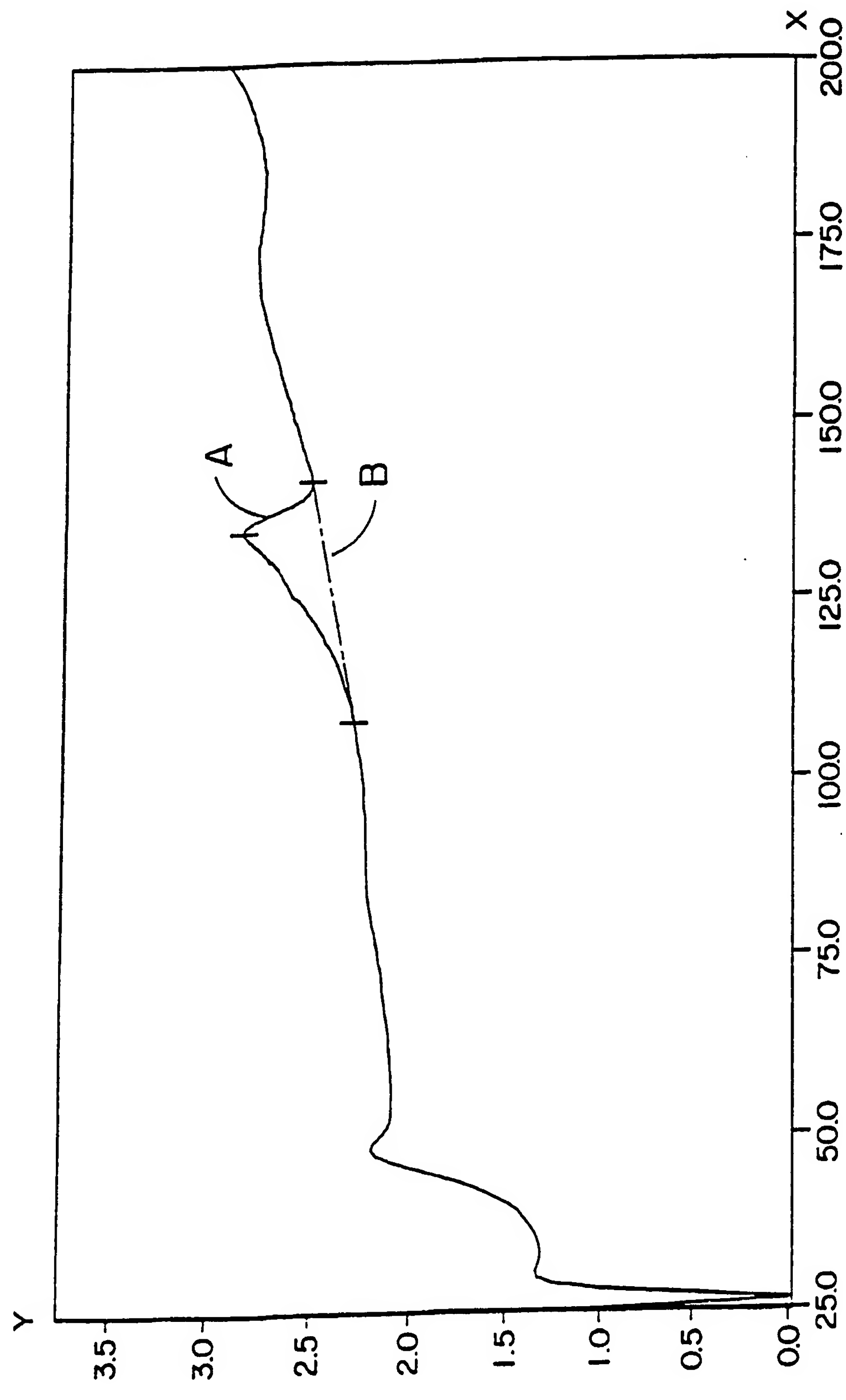


FIG. 9

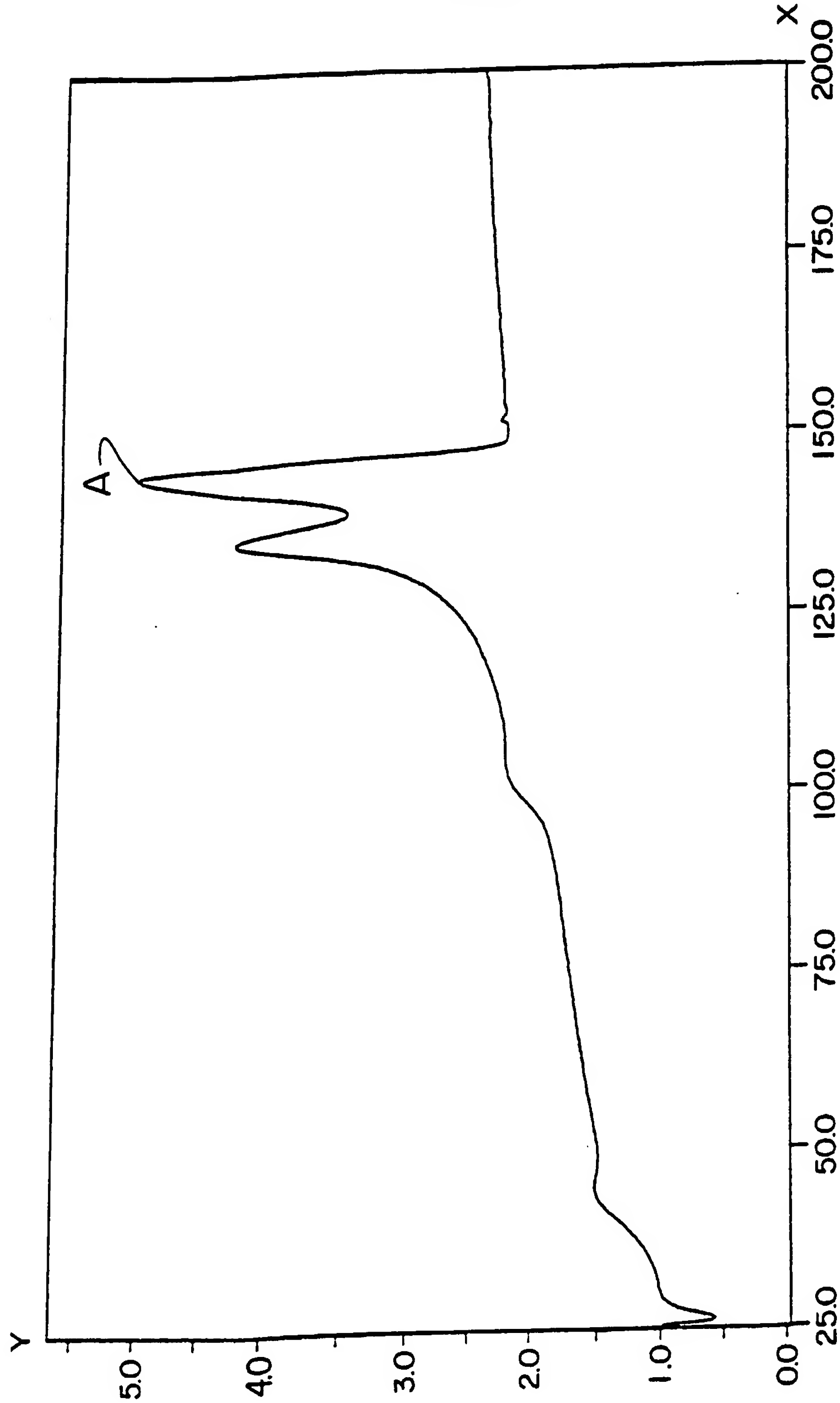


FIG. 10

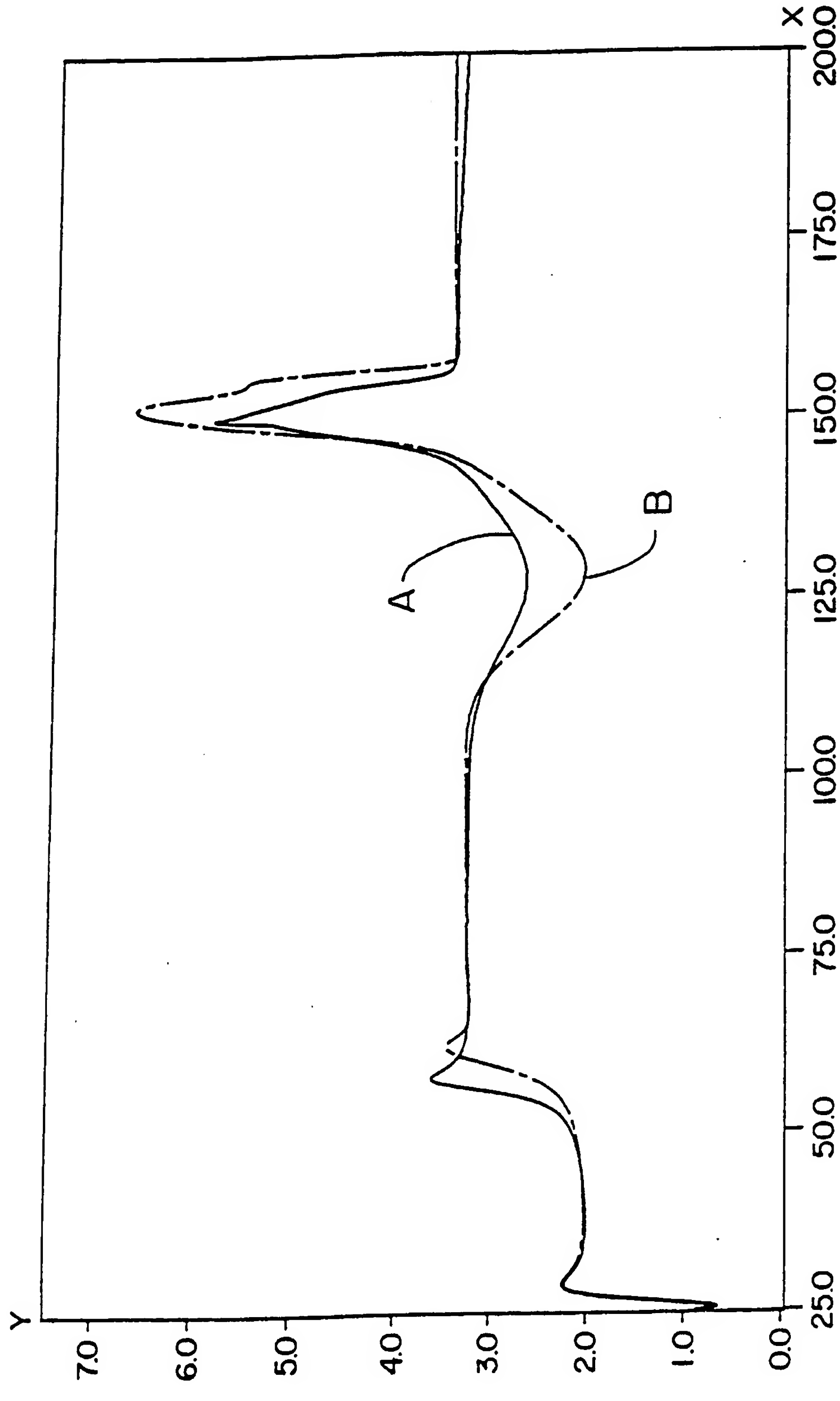


FIG. 11

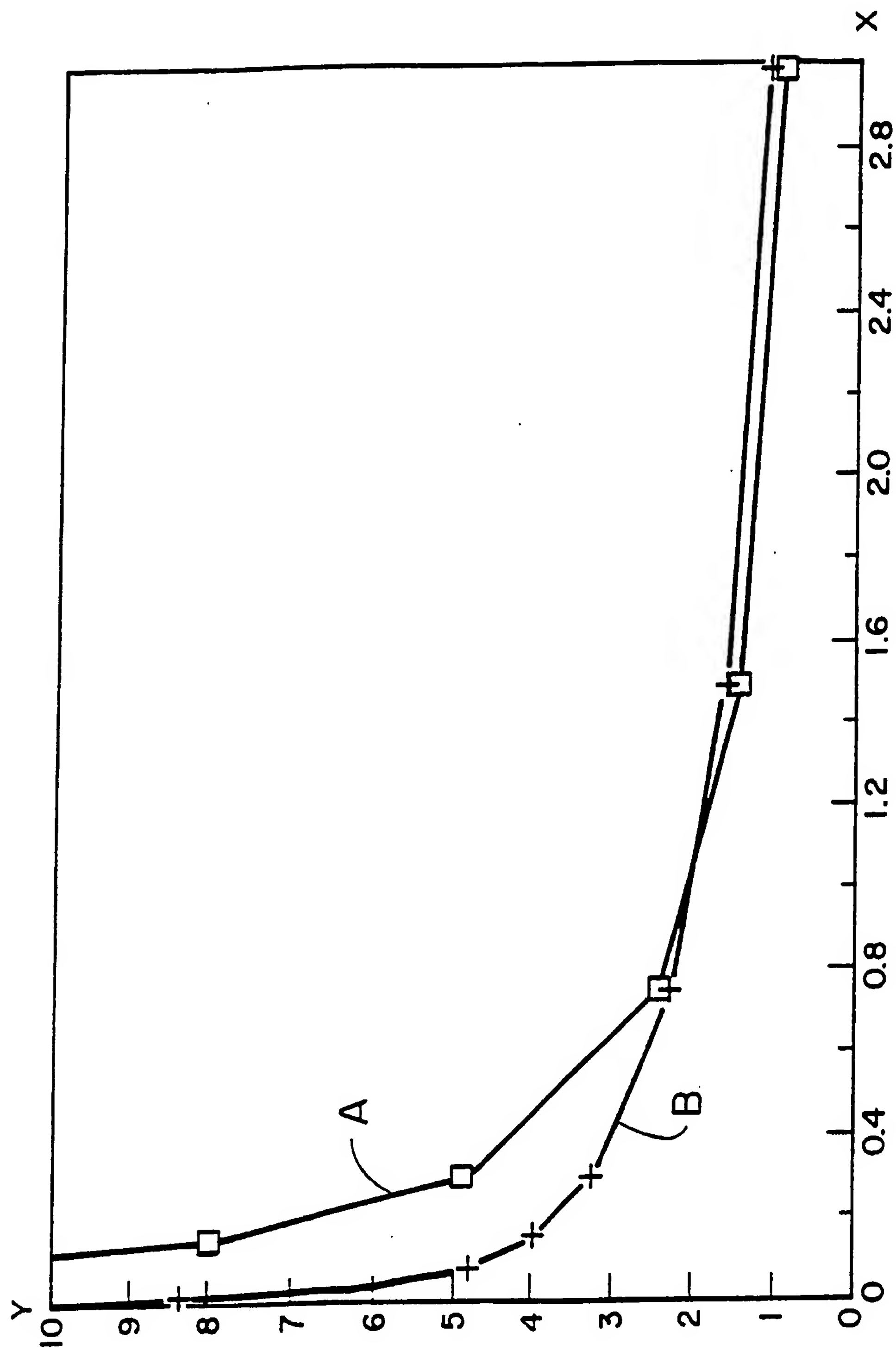


FIG. 12

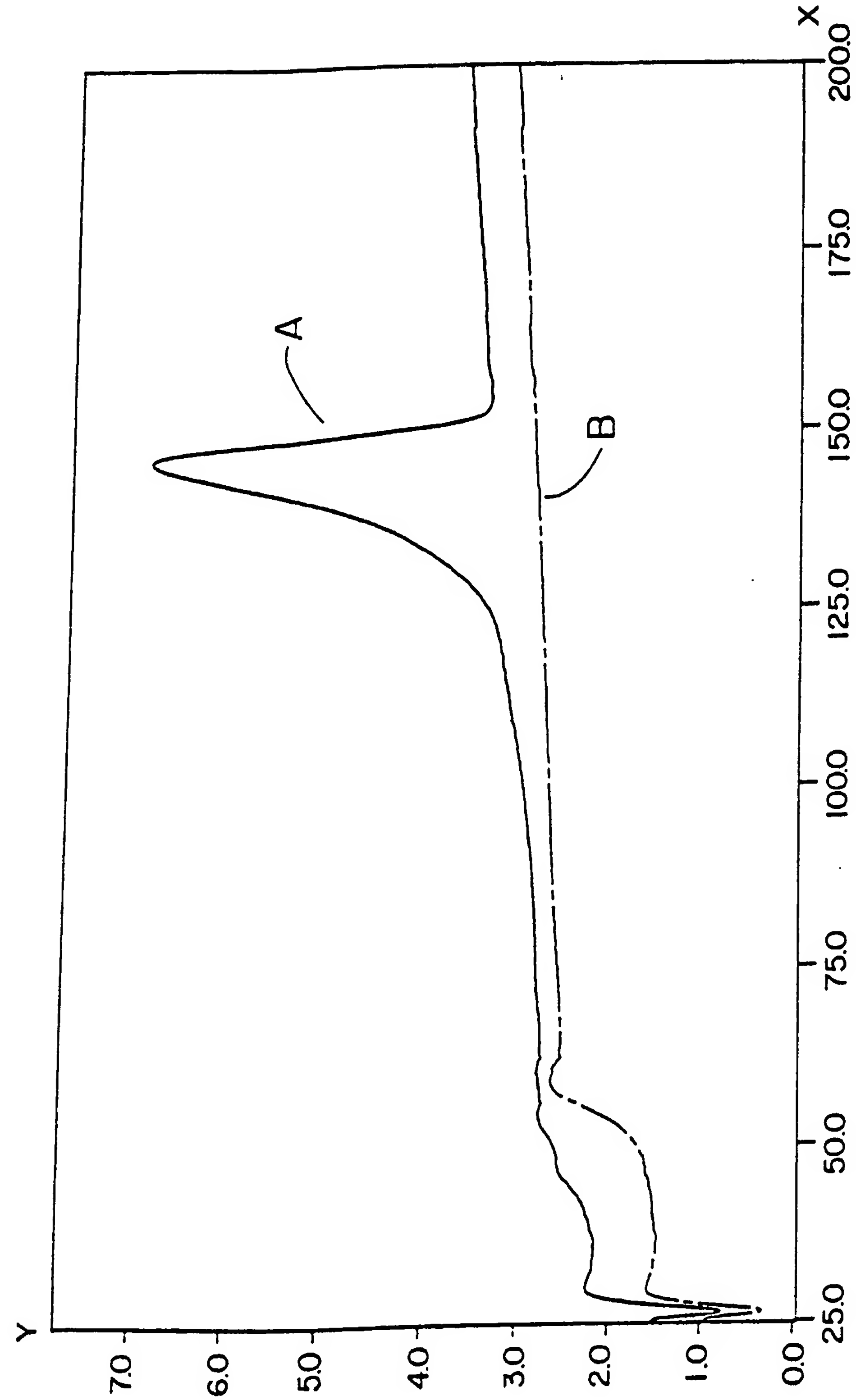


FIG. 13

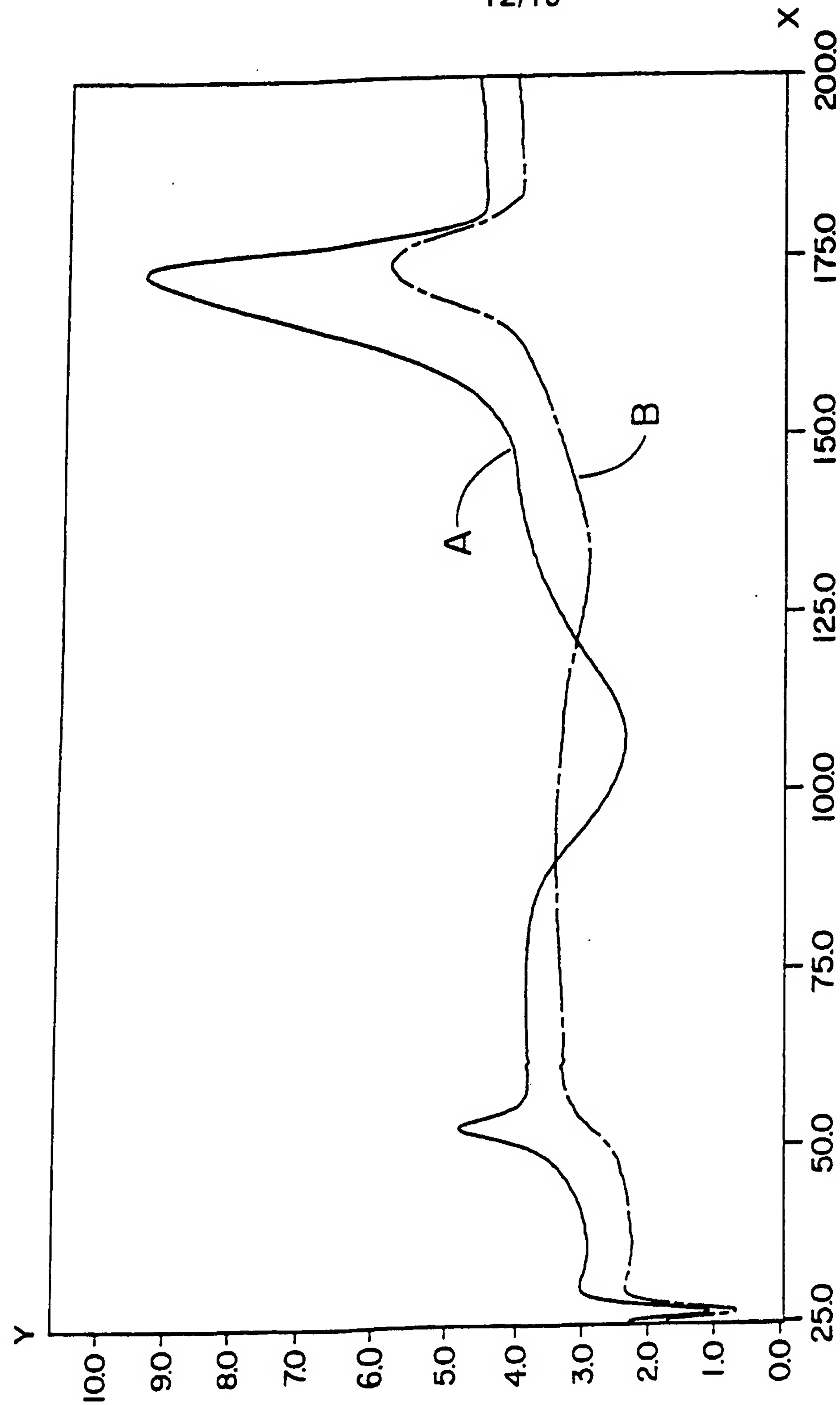

X
Y
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
25.0
50.0
75.0
100.0
125.0
150.0
175.0
200.0
A
B

FIG. 14

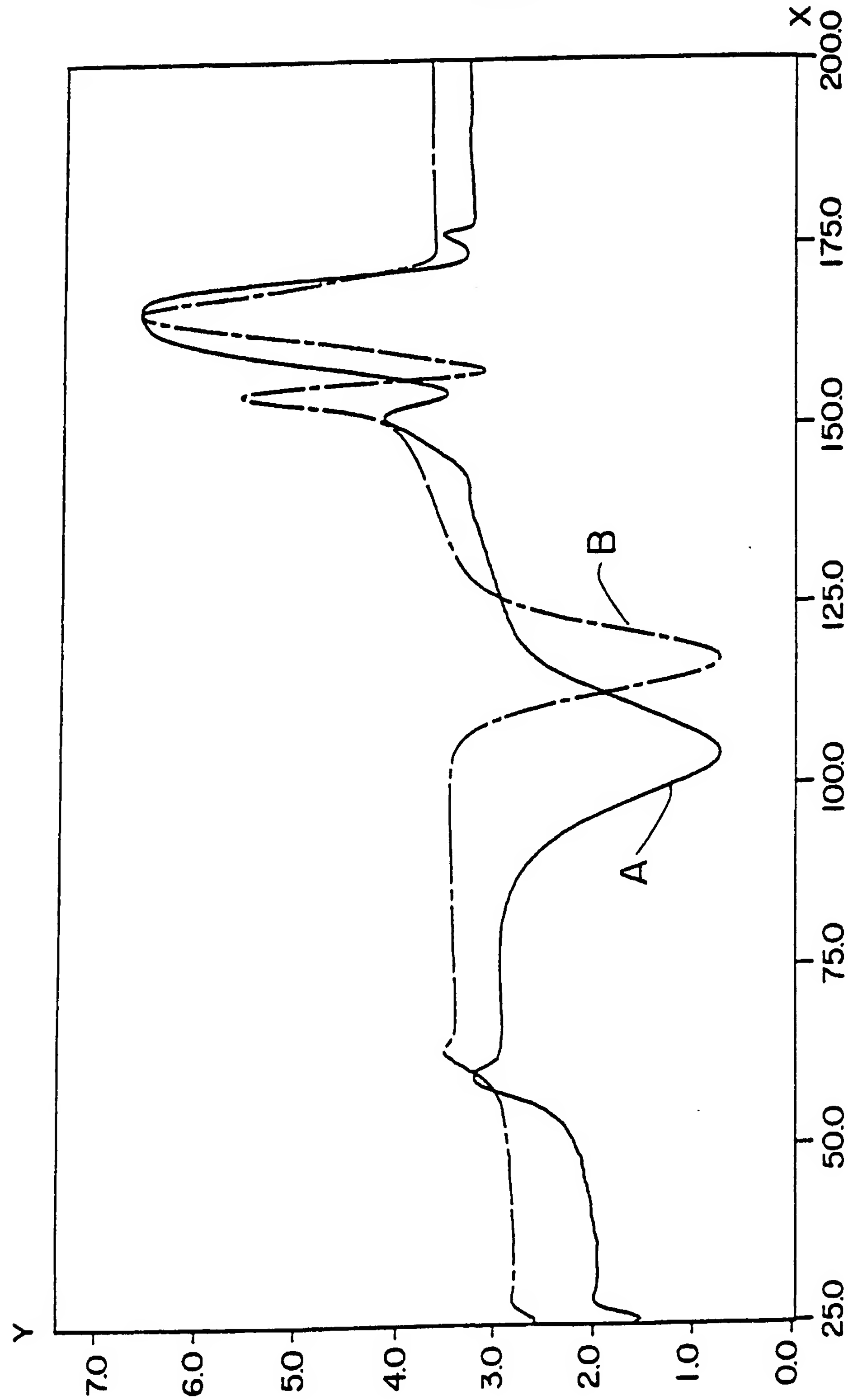


FIG. 15

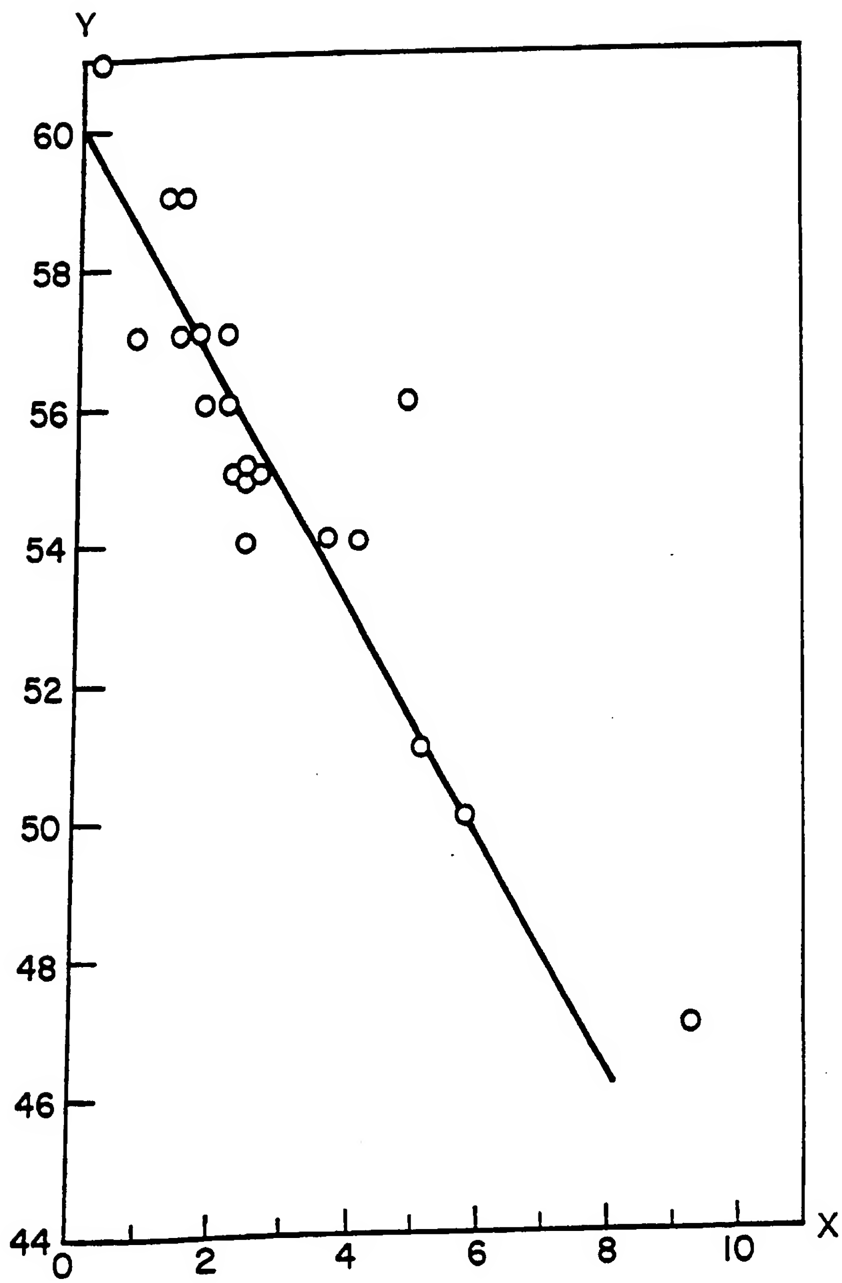


FIG. 16

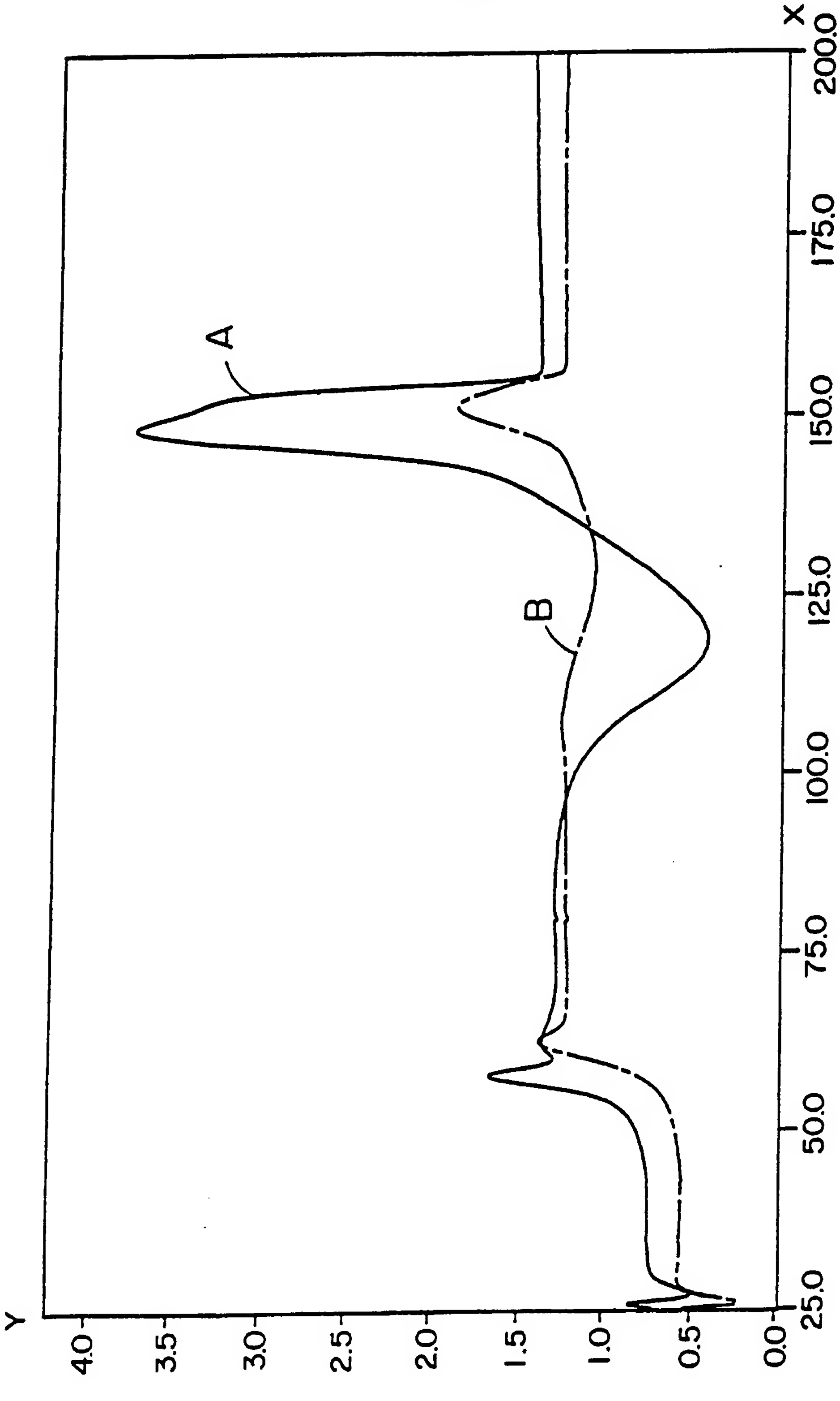

A
B
X
Y
25.0
50.0
75.0
100.0
125.0
150.0
175.0
200.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0

FIG. 17

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/06327

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08L67/04; C08K5/00; C08G63/08; C08J3/18

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C08L ; C08K ; C08G ; C08J

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	WO,A,9 001 521 (BATTELLE MEMORIAL INSTITUTE) 22 February 1990 see claims 1-46 ---	1-14,22, 38,76, 104
A	CHEMICAL ABSTRACTS, vol. 110, no. 24, 12 June 1989, Columbus, Ohio, US; abstract no. 219007F, R. BODMEIER: 'the effect of the addition of low-molecular weight poly(dl-lactide) on drug release from biodegradable poly(DL-lactide) drug delivery systems' page 409 ;column 2 ; & Int. J. Pharm. 1989, 51(1), 1-8 see abstract --- -/--	1-9

° Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
22 JANUARY 1992	-6. 02. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	SIEMENS T.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	CHEMICAL ABSTRACTS, vol. 108, no. 18, 2 May 1988, Columbus, Ohio, US; abstract no. 156432B, T. NAKAMURA: 'surgical application of biodegradable films prepared from lactide-"epsilon"-caprolactone copolymers' page 391 ;column 2 ; & Adv. Biomater. 1987, 7(Biomater. Clin. Appl.), 759-64 see abstract ---	1-9
A	EP,A,0 202 065 (TAKEDA CHEMICAL INDUSTRIES) 20 November 1986 see page 2, line 18 - line 23 see page 3, line 22 - line 28 see page 13 - page 14; example 1 see claim 1 ---	1-134

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9106327 SA 52077

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 22/01/92
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9001521	22-02-90	EP-A- 0428620	29-05-91
EP-A-0202065	20-11-86	JP-A- 62054760	10-03-87
		US-A- 4849228	18-07-89
		US-A- 4728721	01-03-88

EPO FORM P0479

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82